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Methods for Analysis of Organics in Water

Texas Univ. at Dallas, Richardson

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16. ABSTRACT This report describes a laboratory study of liquid-liquid extraction (LLE) method for the analysis of volatile organic compounds in water. The objectives of the study were to examine various method variables, including choice of solvent; solvent to water ratio; matrix pH and ionic strength; and the presence of quenching agents and methanol. The initial phase of the study emphasized optimization of the LLE method for a group of four THMs and other organohalides; but in latter portions of the study, the list of potential analytes was enlarged to include other organohalides and certain aromatics. This necessitated the exploration of capillary chromatographic techniques for the analysis of complex mixtures of the analytes.		
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OPTIMIZATION OF LIQUID-LIQUID EXTRACTION METHODS
FOR ANALYSIS OF ORGANICS IN WATER

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

The research described in this report was carried out to optimize a liquid-liquid extraction procedure for the analysis of volatile organic compounds in drinking water, and so addresses the first of the four objectives listed above.

Robert L. Booth, Acting Director
Environmental Monitoring and
Support Laboratory - Cincinnati

ABSTRACT

This report describes a study of a liquid-liquid extraction procedure for the analysis of volatile organic compounds (VOCs) in water. The method consists of a single-step extraction with *n*-pentane in a closed vial, followed by gas chromatographic (GC) analysis of the compounds in the extract. Several aspects of the procedure have been investigated including extraction efficiencies, precision, accuracy and speed. Solvent: water ratio, pH, and ionic strength of the samples were the principal variables. In initial studies, four trihalomethanes (THMs) were used as analytes, but in later work several other C_1 and C_2 organohalides were added. Subsequently, the method was extended to aromatic compounds such as benzene, toluene, and the xylenes. As the list of compounds grew, packed column GC was found to be inadequate and so open tubular capillary columns were adopted. Combined with electron capture (ECD) and flame ionization detection (FID), capillary columns allow one to use the liquid-liquid extraction procedure for mixtures of these compounds. Method detection limits (MDL) are below 1 $\mu\text{g/L}$ for most organohalides, except for chloroform (2.9 $\mu\text{g/L}$), which was determined by blank values, and haloaromatics and 1,2-dichloroethane (8 $\mu\text{g/L}$), which have low responses to the EC detector. FID method detection limits for aromatics are in the range of 15-40 $\mu\text{g/L}$. Limits of detection may be enhanced by increasing the water:solvent ratio; however, lowered extraction efficiencies ultimately limit this option.

While not without deficiencies, liquid-liquid extraction is a speedy and convenient procedure for the analysis of VOCs in water. The method has been shown to be capable of precise and accurate measurements for the compounds used in this study.

This work was carried out under cooperative agreements CR-805472 and CR-808561 during the period from November 11, 1977 to January 31, 1982. The work was initiated at North Texas State University and transferred to The University of Texas at Dallas in September of 1980, where it was completed. The final report was submitted in May, 1982, received for revision in February, 1983, and submitted in revised form in July, 1983.

CONTENTS

	<u>Page</u>
Foreword	iii
Abstract	iv
Figures	vi
Tables	xi
Acknowledgements	xiv
1. Introduction	1
2. Conclusions	3
3. Background	6
Single-Step Extraction Methods	9
Single-Step Extractions Applied to Analysis of Drinking Water Samples	11
Extraction Efficiencies of Haloalkanes	15
Liquid-liquid Extraction (LLE) for the Analysis of Other Micropollutants in Water	19
Advantages and Disadvantages of the LLE Method for THM and VOC Analysis	20
4. Experimental	23
Materials	23
Procedures	24
5. Results and Discussion	30
Extraction Efficiencies	30
Effect of Sample Constituents on Extraction Efficiencies	44
Choice of Solvent for the LLE Method	53
Effect of Solvent Purity on the LLE Method	56
GC Conditions for the LLE Method	63
Evaluation of the HP 7675A Purge/Trap Module	93
Detection Limits of the LLE Method	104
Applications of the Pentane LLE Method	116
References	127

FIGURES

<u>Number</u>		<u>Page</u>
1	Plots of percent extracted (%E) vs distribution coefficient (D) for some volume ratios (R) between 1 and 1000 where R = volume of water over volume of organic solvent (8)	8
2	Typical chromatogram of THMs plus DBCP by LLE on SE-52 capillary column (29)	17
3	Capillary chromatogram of a standard mixture containing 11 organohalides. Stationary phase, SE-52; 33 m x 0.3 mm 1=CH ₂ Cl ₂ , 2=CHCl ₃ , 3=CH ₃ CCl ₃ , 4=CCl ₄ , 5=CHClCCl ₂ , 6=CHBrCl ₂ , 7=CBrCl ₃ , 8=CHBr ₂ Cl, 9=CCl ₂ CCl ₂ , 10=CHCl ₂ l, 11=CHBr ₃ (19).	18
4	Procedure for removal of water (left) and addition of hydrocarbon (right) prior to LLE/GC	26
5	Survey chromatogram (mixed phase column, 6% OV-11/4% SP-2100) of 9 compound organohalide standard (4 µg/L each) in <u>n</u> -pentane (a) compared to pure solvent injections; (b) <u>n</u> -pentane; (c) <u>n</u> -hexane, (d) <u>isooctane</u> ; (e) methylcyclohexane	57
6	Column blank (a) and standard mixture of VOAs (b) on 10% SP-2100 column. Retention times of standards; 5.45 (CHCl ₃); 7.18 (1,1,1-trichloroethane); 8.52 (CCl ₄); 11.33 (CHBrCl ₂); and CHCl=CCl ₂ ; 22.43 (CHBr ₂ Cl); 27.18 (C ₂ Cl ₄); 36.67 (CHBr ₃). EC attenuation 2 ⁶ ; 2 µL injection	58
7	Survey chromatograms (10% SP-2100 column) of commercial solvents. (a) Fisher pesticide grade <u>n</u> -pentane; (b) Burdick & Jackson pesticide grade <u>n</u> -pentane; (c) Fisher <u>isooctane</u> , redistilled from sodium. EC attenuation 2 ⁶ ; 2 µL injection	59

<u>Number</u>		<u>Page</u>
8	Survey chromatogram (10% SP-2100 column). (a) Aldrich 99% methylcyclohexane. EC attenuation 2^6 ; (b) Mallinckrodt or grade methylcyclohexane. EC attenuation 2^8 . 2 μ L injections . . .	60
9	Survey chromatogram (10% SP-2100 column) of commercial solvents (a) Brudick and Jackson UV grade <i>n</i> -hexane; (b) Mallinckrodt chromar grade <i>n</i> -hexane; (c) Mallinckrodt chromar grade <i>n</i> -hexane after alumina treatment. EC attenuation 2^6 ; 2 μ L injection	61
10	Typical gas chromatogram of 40 μ g/L standard of four THMs with 10% squalane on chromosorb A/AW. Column temperature, 80°; injection port temperature, 100°; Ni ⁶³ EC temperature 300°; attenuation, 2^{12} ; flow rate of helium, 21 mL/min; retention times: 1.43 (CHCl ₃); 2.36 (CHBrCl ₂); 4.30 (CHBr ₂ Cl); 5.29 (1,2-C ₂ H ₄ Br ₂ , internal standard); 8.29 (CHBr ₃)	64
11	Gas chromatogram of finished water extract (1). 2 m x 2 mm i.d. glass column with 3% SP-1000 on Supelcoport (100/120 mesh) at 50°C; 60 mL/min flow rate (5% methane in argon); ECD	65
12	Temperature programmed GC analysis of nine-compound standard with 12.5% squalane on 80/100 chromosorb W/AW. Column temperature: 45°C, 8 min; 1°C/min to end of run	66
13	Temperature programmed GC analysis of nine-compound standard with 3% SP-1000 on 100/120 Supelcoport. Column temperature: 35°, 15 min; 1°C/min to end of run	67
14	Temperature programmed GC analysis of nine-compound standard with 10% SP-2100 on 100/120 Supelcoport. Column temperature: 35°, 14 min; 1°C/min to end of run	69
15	Temperature programmed GC analysis of nine-compound standard with 10% OV-11 on 100/120 Supelcoport. Column temperature: 35°, 15 min; 1°C/min to end of run	70
16	Mixed phase retention time diagram for nine organohalides. <i>tr</i> : retention time; conditions for determining <i>tr</i> given in text	72

<u>Number</u>		<u>Page</u>
17	Temperature programmed GC analysis of nine-compound standard on mixed phase column containing 8% SP-2100, 2% OV-11 on 100/120 Supelcoport. Column temperature: 35°, 14 min; 2°C/min to end of run. .	74
18	Temperature programmed GC analysis of nine-compound standard on mixed phase column containing 6% OV-11 and 4% SP-2100. Column temperature: 45°, 12 min; 1°C/min to 70°C	75
19	Chromatogram of nine-compound organohalide mixture on glass WCOT column with 3:2 OV-11/SP-2100. Code in table 23; conditions in text	76
20	⁶³ Ni electron capture gas chromatogram of volatile organic compound standard. Code listed in table 24; WCOT glass column with SE-54; 60 m x 0.25 mm i.d.; purge delay for splitless injection: 0.5 min: septum purge, 4 ml/min; inlet purge, 70 ml/min; temperature program: 0°C, 1 min; 3°/min to 110°C; helium carrier gas velocity, 31 cm/sec at 0°C; make-up gas to detector, 50 mL/min Ar/CH ₄	77
21	Flame ionization gas chromatogram of volatile organic compound standard, SE-54 capillary column. See table 24 for compound code and figure 20 for conditions (helium rather than Ar/CH ₄ to detector). 78	
22	Fused silica capillary column chromatography (SE-54) of the four trihalomethanes in n-pentane and internal standard (see table 23 for code and text for conditions). Right: 40°C, isothermal; left: 40°C, 3 minutes; 3°C/min to end of run (X= solvent impurity).	81
23	Fused silica capillary column chromatograph (SE-54) of the four trihalomethanes in n-pentane and internal standards (see table 23 for code and text for conditions. Right: initial temperature, 20°C; left, 30°C	82
24	Fused silica capillary column chromatograph (SE-54) of volatile organohalide mixture in n-pentane. Initial temperature, 20°C. Other conditions in text; code in table 23	84
25	Fused silica capillary column chromatograph (SE-54) of volatile organohalide mixture in n-pentane. Initial temperature, 0°C. Other conditions in text; code in table 23	85

<u>Number</u>		<u>Page</u>
26	Fused silica capillary chromatograms (SE-54) of two mixtures of commercial grade <u>cis</u> - and <u>trans</u> -1,2-dichloroethylene plus 1,2-dichloroethane in <u>n</u> -pentane. Conditions as in figure 25	87
27	Fused silica capillary column chromatogram (SE-54) of a mixture of aromatic hydrocarbons in <u>n</u> -pentane. Conditions same as figure 16; code in table 23. Flame ionization attenuation, X2. Concentrations 2 ng/ μ L	89
28	Fused silica capillary column chromatogram (SE-54) of a mixture of volatile organohalides, FID attenuation X2. Code in table 23; conditions same as figure 16. Conditions 2 ng/ μ L	90
29	Electron capture purge and trap chromatogram of reagent water (a) and organohalide mixture (b) Hewlett-Packard 7675A purge and trap module with ^{63}Ni ECD. Code in Table 26; conditions in text	94
30	Response of the ECD to chloroform concentrated with the HP 7675A purge and trap module.	95
31	Response of the ECD to tetrachloroethylene and carbon tetrachloride concentrated with the HP 7675A purge and trap module	96
32	Response of the ECD to bromoform (upper curve) and bromodichloromethane and chlorodibromomethane (lower curve) concentrated with the HP 7675A purge and trap module	97
33	Response of the ECD to 1,2-dichloroethane (upper curve) and 1,1,1-trichloroethane, trichloroethylene, and <u>trans</u> -1,2-dichloroethylene (lower curve) concentrated with the HP 7675A purge and trap module	98
34	Flame ionization, purge and trap chromatogram with HP 7675A module (a) water blank; (b) standard mixture (table 27)	100
35	Schematic diagram showing regions of detection and quantitation of an analytical method. LOQ = limit of quantitation; LOD = limit of detection (method detection limit, MDL), Sb = signal level in blank; σ = standard deviation of blank [from "Data Acquisition and Data Quality Evaluation in Environmental Chemistry", Amer. Chem. Soc. (25)] .	102

Number

Page

36	Sensitivity plot for GC analysis of 1,2-dichloro-ethane in pentane (GC conditions as in figure 25)	114
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TABLES

<u>Number</u>		<u>Page</u>
1	Extraction efficiencies and partition ratio for LLE	7
2	Extraction efficiencies of haloalkanes in purified water using hydrocarbon solvents	13
3	Extraction efficiencies of haloalkanes in waste- water using <u>n</u> -pentane solvent ($V_w/V_s = 100$)	14
4	Recovery of volatile organohalides by micro- extraction	16
5	Recovery of haloalkanes at 1000 $\mu\text{g/L}$ from water containing different amounts of methanol . . .	16
6	LLE extraction efficiencies (20:1) in organic free water	31
7	LLE extraction efficiencies (20:1) in organic free water	33
8	LLE extraction efficiencies (20:1) of nine volatile halides from Denton tap water	35
9	LLE extraction efficiencies (20:1) of nine volatile halides from Denton tap water	36
10	Partition coefficients for VOCs in water: <u>n</u> -pentane ($V_w/V_w = 20$)	37
11	Effect of pH and ionic strength (μ) upon pentane LLE efficiency of chloroform in water	38
12	Effect of pH and ionic strength (μ) upon pentane LLE efficiency of bromodichloromethane in water .	39

<u>Number</u>		<u>Page</u>
13	Effect of pH and ionic strength (μ) upon pentane LLE efficiency of dibromochloromethane in water	41
14	Effect of pH and ionic strength (μ) upon pentane LLE efficiency of tetrachloroethylene in water . .	42
15	Effect of pH and ionic strength (μ) upon pentane LLE efficiency of bromoform in water	43
16	Effect of ionic strength (μ) upon pentane LLE efficiency (20:1) of five volatiles in water . . .	45
17	Effect of ionic strength variations upon Denton tap water spiked with five volatiles	47
18	Effect of ionic strength upon extraction of four volatiles in purged Denton tap water	49
19	Effect of sodium sulfite upon extraction by LLE of four volatiles in Denton tap water	50
20	Effect of methanol upon the extraction of four volatiles by LLE	54
21	Purity of solvents obtained from various suppliers .	67
22	Retention times for nine compounds on squalane and a mixed phase packing	73
23	Code for compounds analyzed by capillary GC	80
24	Retention times of organic compounds on SE-54 FSOT column	86
25	Purge and trap analysis of organohalides with the HP 7675A module	103
26	Purge and trap analysis of aromatic hydrocarbons with the HP 7675A module	106
27	Signal/noise estimation of LLE detection limits by ECD	107
28	LLE method detection limits determined by reagent blank with ECD	108
29	MDLs by capillary GC/LLE method organohalides ($\mu\text{g/L}$)	110

<u>Number</u>		<u>Page</u>
30	MDLs by capillary GC/LLE aromatics (ug/L)	111
31	120:0.5 LLE method: estimated detection limits . .	112
32	Precision of LLE method for trihalomethanes in actual water samples	119
33	Variance and precision of replicate capillary GC analysis of spiked standards of organohalides in water	121
34	Analysis of EPA quality control check sample #WP 1278 by the pentane LLE method with FSOT capillary GC analysis	122
35	LLE/capillary GC and purge and trap analysis of drinking water samples	125
36	Purge and trap-ECD analysis of EPA drinking water samples - effect of dilution	126

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SECTION 1

INTRODUCTION

The analysis of volatile organic compounds (VOCs) in drinking water is now mandated by regulations proceeding from the passage of the Safe Drinking Water Act of 1974. At the present time maximum contaminant levels (MCLs) are in effect for four trihalomethanes (THMs), and an Advance Notice of Proposed Rulemaking has been published for fourteen other VOCs (1,2). Several analytical methods are available which potentially have the required precision, accuracy and sensitivity to monitor these compounds at the $\mu\text{g/L}$ level (1-6). Each of these methods utilizes gas chromatography (GC) for separation and quantification of the analytes, with the choice of detector depending on the particular compound and concentration level. One of the approved methods for monitoring THMs consists of a single-step liquid-liquid extraction (LLE) procedure, sometimes called microextraction, in which 10 mL of water is extracted in a small, closed vial with 2 mL of *n*-pentane (1). The pentane layer is then sampled with a microliter syringe, and an aliquot injected into a gas chromatograph with a packed column and an electron capture detector (ECD). The method is relatively fast, precise and capable of detecting THMs below 1 $\mu\text{g/L}$.

The extension of the LLE method to the analysis of other VOCs was one objective of this research. Several approaches have been used, principally the optimization of the ratio of solvent to water volume; the use of capillary columns; and programmed temperature control for more efficient GC separation; and various changes in the type of extraction vessel and methods of mixing the solvent and water.

A second objective of this work was to investigate the effects of pH and salt upon the efficiency of the LLE process.

A final objective was to compare the LLE procedure with a purge and trap method using samples taken from actual drinking water sources.

The results of these studies show that LLE is an excellent method for the analysis of THMs and several other chlorinated organic compounds of low molecular weight. The lower limit of detection is primarily determined by the solvent:water ratio and

the electron capture cross section of the analyte. Ionic strength effects have been shown to be minimal over the range of ionic strengths found in drinking water. Higher quantities of salt may be added to enhance the extraction efficiency, if desired. The effect of pH on the extraction process is negligible, at least for the VOCs studied in this work.

The extension of the LLE procedure to the analysis of mixed chlorinated and non-chlorinated VOCs may require: (a) the use of EC and FID detectors; (b) a solvent of either very high or very low volatility which will be eluted before or after the analytes; (c) cryogenic temperature programming of the GC if a very volatile solvent is used; and (d) capillary GC methods with either glass or fused silica columns. Lower limits of detection of non-chlorinated (aromatic) hydrocarbons are generally greater than the chlorinated C₁ and C₂ compounds used in this work.

Relative advantages and disadvantages of the LLE procedure vis a vis the purge and trap method are discussed in the context of results of actual drinking water samples analyzed by the two methods.

SECTION 2

CONCLUSIONS

The pentane LLE procedure described in this work appears to be a precise and accurate method for the analysis of volatile organohalides and certain aromatic compounds in drinking water.

The method, which utilizes a 20:1 volumetric ratio of water sample to solvent, gave extraction efficiencies which were independent of pH from 4 to 10, independent of ionic strength below 0.5 M NaCl, independent of Na_2SO_3 below 126 mg/L and independent of added methanol below 1%.

In conjunction with the recommended extraction procedure, a variety of gas chromatographic conditions were used for the analysis of organohalides and aromatics.

For the analysis of trihalomethanes (THMs), packed GC columns give satisfactory separation. A variety of liquid phases may be used to accomplish the separation of THMs, including squalane, SP-1000, SP-2100. For routine work, 10% squalane packed on a suitable support (Supelcoport 100/120 mesh) is recommended. The column should be glass, with typical dimensions of 9 ft. x 2 mm i.d. For confirmation purposes, a column of different polarity should be used, such as one containing the SP-1000 phase. Another confirmation column used in this work contained 6% OV-11 and 4% SP-2100. THM analysis may also be accomplished by capillary column GC. In this work, a fused silica column with SE-54 liquid phase gave excellent resolution, as did a glass SE-54 column and a glass column with a 3:2 mixture of OV-11 and SP-2100. With splitless injection, an initial column temperature of 20°C or lower was required to obtain the good solvent effect required for precise quantification. For most sensitive analyses, the ECD is recommended for THM analysis, although FID is possible if higher detection limits can be tolerated.

Some volatile organic halides other than THMs may be separated adequately using packed column techniques. Squalane, OV-11, SP-2100 and SP-1000 columns were found to be inferior in this respect to the 6% OV-11/4% SP-2100 mixed phase column. Even

with this column, resolution was marginal, especially of 1,2-dichloroethane from CCl_4 , and GC analysis times are in excess of 30 minutes for CHBr_3 . Volatile organohalides were separated with greater efficiency using high performance glass or fused silica capillary columns with wall coating. In this work, capillary columns were evaluated using the Grob-type splitless injection technique, which was found to give good resolution and good precision. Glass and silica columns with SE-54 wall coating gave adequate separation of several volatile organohalides. Although not evaluated as thoroughly, the OV-11/SP-2100 (3+2) glass WCOT column appeared to give superior separation compared to the SE-54 columns. Again, because of the need for a good solvent effect, *n*-pentane solutions must be analyzed starting at a column temperature 10-20 degrees centigrade below the boiling point of the solvent. For separation of 1,2-dichloroethane from 1,1,1-trichloroethane, an initial temperature of 0° was found to be optimal. The column temperature regime finally used was 0° for three minutes, followed by an increase of 3°C/min. to the end of the run. Under these conditions, baseline separation of ten organohalides was achieved and bromoform eluted at approximately 23 minutes on the 30 meter SE-54 FSOT column. Additional organohalides with retention times in excess of bromoform may also be analyzed by the same procedure, as illustrated by *o*-dichlorobenzene (31 minutes elution time). Very volatile organohalides such as the mono- and dichloroethylenes are difficult to analyze in *n*-pentane by the splitless WCOT technique. While not tried in this work, a separate extraction using a more volatile solvent might be successful, albeit not with the splitless injection technique. The ECD is preferred for organohalides, but for certain compounds the sensitivity is lower than one may require for environmental analyses.

Volatile aromatic hydrocarbons such as those listed in Table 22 may be analyzed by the LLE/GC method. In this work, only WCOT columns were used, namely the SE-54 glass and fused silica columns. Some retention time redundancies were observed with these columns (*m*- and *p*-xylene; styrene and *o*-xylene), but detectability is good with the FID. The sharpness of the peaks in this mode indicated that there is less dead volume in the FID as compared to the ECD.

Detection limits of the pentane LLE method using packed column and FSOT capillary column techniques were determined. For the brominated THMs, MDL values are in the range of 0.6 - 0.8 µg/L; but for chloroform, and MDL of near 3 µg/L is indicated. This is due to variations in blank levels in pentane and in water used for preparing calibration standards. Other organohalides have MDL values in the range of 0.2 - 0.6 µg/L except for 1,2-dichloroethane whose MDL is determined by an

artifact in the blank at 8 $\mu\text{g/L}$. 1,2-Dichloroethylene may have a similar high level that was not detected in this study. 1,2-Dichlorobenzene, an example of a compound not currently under active consideration as a drinking water contaminant (2), may also be determined by the 20:1 LLE/GD-ECD method with an MDL of 2 $\mu\text{g/L}$. Aromatic compounds determined with the FID have somewhat higher MDL values, ranging from 16 to 40 $\mu\text{g/L}$. Lower MDL values may be achieved with a higher water or solvent extraction ratio, such as the 240:1 method described in this work. The method has not been thoroughly tested or optimized, and should be used only after appropriate development work.

The precision of the 1:20 pentane LLE method as practiced in this work was usually within $\pm 20\%$. Two EPA Quality Check (QC) samples containing nine volatile organohalides were analyzed by the LLE method with capillary FSOT/GC columns. Except for 1,2-dichloroethane and in one case for bromoform, reported values were within 18% of the true values. Average variance from the true value was $\pm 6\%$ for the low concentration sample (excluding 1,2-dichloroethane), and ± 13 (including all nine compounds) for the high concentration sample.

Analysis of five samples of water supplied by EPA was carried out by the LLE method with FSOT/GC and by the purge and trap (Purge/trap) method with EC and FI detectors. In general, the results obtained by the two methods were close to each other, with a few notable exceptions. With the ECD, the Purge/trap module is so sensitive for organohalides that dilutions of the samples were required. This is a laborious procedure which may result in poor precision and accuracy in some cases. No hydrocarbons were observed by LLE, but benzene was quantified at 7 $\mu\text{g/L}$ in one sample by Purge/trap:FID.

SECTION 3

BACKGROUND

LLE has been used for many years as a concentration method in schemes for the analysis of organic compounds from environmental samples. The method consists of extraction of the desired analyte(s) from the sample by an organic solvent. For water samples, the extraction is usually carried out by mixing water and an immiscible solvent in a separatory funnel, followed by separation of the layers. The organic solvent is chosen on the basis of its ability to efficiently extract the desired solute(s) from water; a relatively low boiling point (for ease of evaporation); and low solubility in water.

THERMODYNAMICS OF LLE

After a single extraction step, the ratio of the concentration of the solute i (analyte) in each phase is defined as the partition coefficient (also referred to as partition ratio or distribution coefficient), K_D (7)

$$K_D = \frac{[i]_s}{[i]_w} \quad \text{Eq. (1)}$$

where $[i]_s$ and $[i]_w$ represent the concentrations of solute i in the organic solvent phase and water phase respectively.

The fractional extraction efficiency f is defined as the fraction of the mass of solute in the organic solvent phase after extraction:

$$f_i = \frac{m_{i,s}}{m_{i,s} + m_{i,w}} = \frac{m_{i,s}}{m_{i,T}} \quad \text{Eq. (2)}$$

where $m_{i,s}$ and $m_{i,w}$ are masses of solute in solvent and water phases respectively and $m_{i,T}$ is the total mass of solute. Equation (2) may be converted to equation (3) by substitution of concentration terms for masses, i.e.,

$$f_i = \frac{[i]_s \cdot V_s}{[i]_s V_s + [i]_w \cdot V_w} \quad \text{Eq. (3)}$$

where V is the volume of the respective phase. Rearrangement of equation (3) and substitution of equation (1) gives

$$f_i = \frac{1}{1 + (1/K_D) \cdot (V_w/V_s)} = \frac{K_D}{K_D + V_w/V_s} \quad \text{Eq. (4)}$$

Equations (2) and (4) are the basis for calculating values of the extraction efficiency and the partition coefficient from experimental data. Usually this involves the evaluation of f from the determination of the amount of component i in the organic phase and then the calculation of K_D from equation (4). Table 1 shows values of f for various values of K_D and at three different volumetric ratios, $V_w/V_s = 20$ and 100, and 1000.

TABLE 1. EXTRACTION EFFICIENCIES AND PARTITION RATIO FOR LLE [reference equation (2)].

K_D	f		
	$V_w/V_s = 20$	$V_w/V_s = 100$	$V_w/V_s = 1000$
10^{-2}			
10^{-1}	0.00050	0.000010	0.0000010
10^0	0.0050	0.00010	0.000010
10^1	0.048	0.0099	0.00010
10^2	0.33	0.090	0.0099
10^3	0.83	0.50	0.091
10^4	0.98	0.91	0.50
	0.99	0.99	0.91

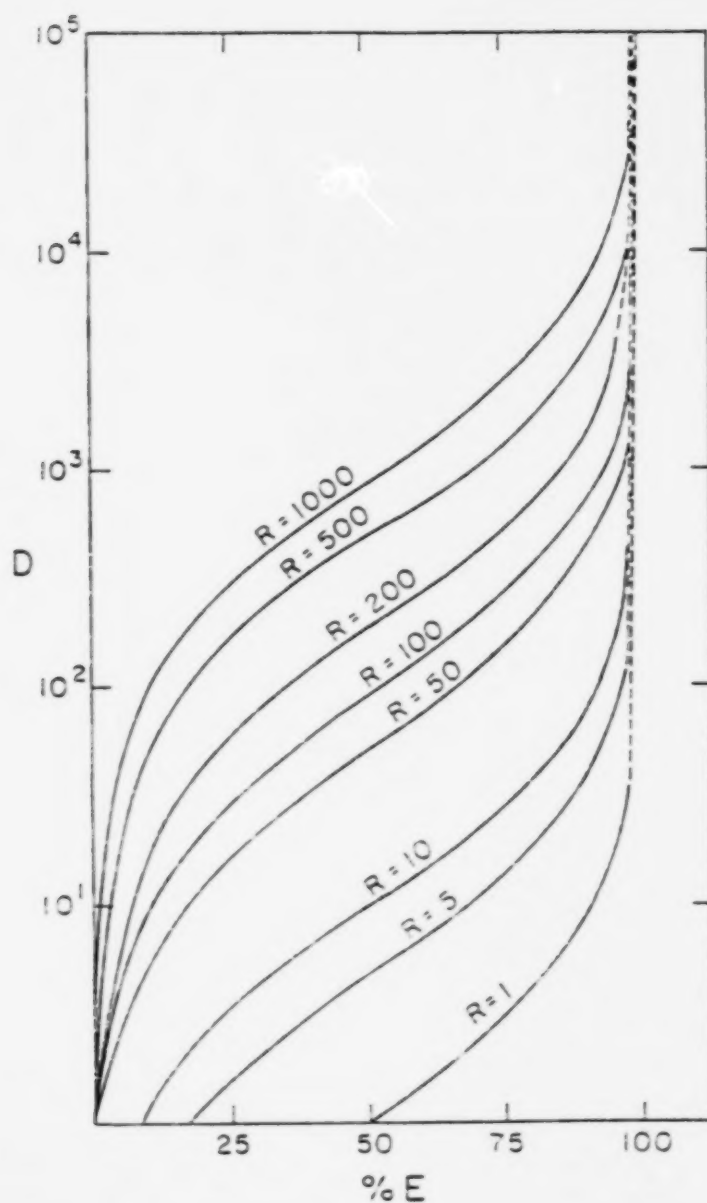


Figure 1. Plots of percent extracted (%E) vs. distribution coefficient (D) for some volume ratios (R) between 1 and 1000 where R = volume of water over volume of organic solvent. (Taken from reference (8) with permission of Ann Arbor Science Publishers, Inc., Ann Arbor, MI.)

It is apparent from equation (2) and Table 1 that the extraction efficiency increases as the partition ratio increases and decreases as the volumetric ratio V_w/V_s increases. Figure 1 is a plot of the percent extraction efficiency at various volumetric ratios V_w/V_s and with different distribution coefficients, taken from Junk *et al.* (8). Plots of this type have also been used by Rhoades and Nulton (9) to illustrate the effect of these two variables on extraction efficiency.

SINGLE-STEP EXTRACTION METHODS

As noted above, LLE is usually carried out by multiple extractions using separatory funnels. This approach is preferred by many in order to achieve nearly quantitative recovery of the analytes. In addition, if a sample of about one liter size is extracted with a volatile solvent, after extraction the solvent may be partially evaporated to give a large concentration factor. However, as Rhoades and Nulton have observed (10), this procedure suffers from several liabilities; namely:

1. the possible loss of analyte during the manipulation steps, including particularly,
2. the loss of very volatile compounds in the evaporative concentration step which usually follows extraction; and
3. the possibility of sample contamination.

For these reasons, and because of the desire for a more simple procedure, several groups of analysts have promoted the use of a single extraction step (3,4,8,9,10-21). Several variations of this method have been used in which volumetric ratios V_w/V_s range from 5 (15) to 4900 (21).

Rhoades and Nulton were probably the first to publish a single-step extraction/GC procedure, using the method to analyze fruit flavor components after steam distillation (11). Grob *et al.* (4) were the first to apply such a method to the analysis of drinking water. Subsequently, single-step extraction/GC has been used for the analysis of priority pollutants in wastewater effluents (9,10,18); pesticides (12,20,21); THMs and other volatile organohalides (14-19); and polynuclear aromatic and other hydrocarbons (4,8,9).

A single-step extraction/GC method has recently been approved for the analysis of four THMs: CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 , in drinking water (1). The method, an adaptation of one by Mleure (15), uses a volumetric ratio of only 5, which is

possible because of the high sensitivity of ECDs for these compounds. The extraction efficiency under these conditions is nearly quantitative, thereby avoiding the common criticism of the single-step extraction procedure, *i.e.* low recovery efficiencies.

Most applications of the single-step extraction/GC method have used higher volumetric ratios, usually from 20:1 to 100:1. Grob *et al.* (4) and Murray (21) even used ratios of 4000-5000; that is, with one liter of water and 200-250 μ L of solvent. Critics point out that extraction efficiencies under these conditions are often lower than the 60% limit, which is usually held to be desirable for an extraction method (22). Responding to this criticism, Rhoades and Nulton (9) have pointed out that single-step extraction/GC methods often give overall extraction efficiencies comparable to standard, multiple-step methods. This is true because the single-step methods avoid the problems outlined earlier in this section, *i.e.* contamination and solute losses. Moreover, they point out that the addition of salt in the single-step procedure will increase extraction efficiencies appreciably.

More importantly, Rhoades and Nulton emphasized that an analytical method which involves a separation step need not involve nearly quantitative recovery of the analytes: If an analytical approach leads to only a 30-60% recovery, but does so consistently, reliable data can still be obtained (10).

To confirm this position, Rhoades and Nulton (10) compared their single-step extraction method with procedures for priority pollutants used in the effluent guidelines verification phase (23). Sample volumes were 10-100 mL and 200-1000 μ L of solvent were used, usually with NaCl added to saturation. In general, single-step extraction efficiencies and precision compared favorably with EPA-approved methods, although test compounds generally had high K_D values.

In addition to Rhoades and Nulton, Murray (21) also tested single- and multi-step extraction/GC procedures for the analysis of priority pollutant "extractables". Water and solvent volumes of 980 mL and 200 μ L respectively were used; *i.e.* V_w/V_s a procedure similar to Grob *et al.* (4). This method was compared to two continuous extraction methods which were designed to give near quantitative recoveries. Tap water spiked with several hydrocarbons and pesticides was analyzed by the single-step method and the two continuous methods. The extraction efficiencies by the single-step method averaged only 58% with standard deviations ranging from 2.9 to 10.3%, with the higher value at the 10 ng/L for four pesticides. Unfortunately, no precision or efficiency data were reported on the continuous

extraction procedures.

Thrun and Oberholtzer (18) evaluated the single-step method using a 90 mL aliquot of sample extracted with 5 mL and 1 mL of n-pentane. In some samples Na_2SO_4 was used to saturate the aqueous layer in order to improve extraction efficiencies. Both "clean" water and a latex wastewater were used as the matrix. Benzene, toluene, o-xylene, ethyl benzene, phenols and phthalates were the test compounds, though not all combinations of test compound and matrix were used. Again, reproducible results were obtained, even where recoveries were not high.

To be sure, in each of these studies the test compounds were those with relatively large partition coefficients. While Rhoades and Nulton (10) used their method to analyze wastewater for a series of halogenated C_1 and C_2 alkanes, some of which have lower partition coefficients, a direct comparison with the purge/trap method was unfortunately not given. Nonetheless, for spiked samples, percent recoveries averaged 72% with a range from 62% (dibromochloromethane) to 97% (1,1,2,2-tetrachloroethane). Standard deviations of replicate analyses of these compounds averaged 19% with a range from 14% (chloroform, carbon tetrachloride, 1,2-dichloropropane and 1,1,2-trichloroethane) to 29% (dibromochloromethane). Actual wastewater samples were analyzed in duplicate for chloroform, trans-1,2-dichloroethylene, 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene. Variabilities, defined as the absolute difference between duplicates expressed as percent of mean value $[(X_1 - X_2)/X] \times 100$, averaged 14% with a range from 7% (1,2-dichloroethane) to 19% (trans-1,2-dichloroethylene). Concentrations of the spikes or compounds found in the wastewater samples were not given, nor were direct comparisons made between the single-step extraction method and an EPA-approved procedure.

SINGLE-STEP EXTRACTIONS APPLIED TO ANALYSIS OF DRINKING WATER SAMPLES

Grob et al. analyzed tap water spiked with diesel oil and a mixture of VOCs to demonstrate the relative advantages of LLE and closed loop stripping (4). Under their conditions, $V_w/V_s = 4000$, very low extraction efficiencies were realized (15-45%), but the method still gave good results.

Henderson et al. (14) developed a single-step LLE procedure for the analysis of THMs in drinking water. An important contribution of this method was the use of a 120-mL vessel which served both for collection of the sample and the extraction steps. Moreover, with the use of a Teflon-lined silicone septum in the cap, the addition and removal of solvent could be

accomplished without opening the vessel. The volumetric ratio V_w/V_s was 120:5, later modified to 120:3, and the solvent used was n-pentane.

Subsequent to this report, Mieure (15) and Richard and Junk (16) reported two other single-step LLE procedures for THM analysis. Mieure's procedure involved a volumetric ratio of 5:1 with methycyclohexane as the specified solvent. The procedure was carried out by adding 1.0 mL of solvent and 1.5 of NaCl to a 2-dr vial, followed by 5.0 mL of water sample. The vial was closed and shaken vigorously for one minute, and the THMs analyzed by GC/EC with a 3% OV-1 liquid phase.

Richard and Junk (16) reported a similar procedure which used 10 mL of water and 1 mL of n-pentane using 15-mL glass-stoppered and calibrated centrifuge tubes or volumetric flasks. Isooctane was proposed as an alternative solvent which would elute after, rather than before the THMs. Both ECD and FID were used for the analytical step.

The EPA-approved procedure (1) for analysis of THMs by LLE is a modification of the Mieure procedure (15). The method recommends n-pentane as the solvent; but others may be used when laboratory temperatures or altitude are too high for the safe handling of n-pentane. A volumetric ratio V_w/V_s of 10:2 is prescribed, with the water being added to a 15 mL vial containing solvent. The vial is closed with a screw cap having a Teflon-lined rubber septum and shaken by hand for one minute.

Reding and coworkers (24) compared the Bellar-Lichtenberg purge and trap procedure (25) with the EPA-approved LLE method using 10 mL of water and 1 mL of methylcyclohexane. The four THMs, trichloroethylene and carbon tetrachloride were resolvable using packed columns with either squalane or Carbowax 1500 liquid phases. Quality control analysis showed that LLE values generally agreed with both the expected and the purge/trap values to within +25% for the THMs. The authors pointed out that the LLE method suffers from two disadvantages; viz. the presence of impurities in the solvent, and the possibility of interfering substances in raw water. Procedures to overcome both problems were outlined.

Eklund, Josephson and Roos (19) used an LLE procedure with 100 mL of water and 5 mL of n-pentane which contained an internal standard CBr_3Cl to enhance the precision of GC analysis. A capillary column GC method was employed as discussed below.

Since the original papers by Grob et al. (4) and Henderson et al. (14), one-step LLE methods have been used by several

TABLE 2. EXTRACTION EFFICIENCIES OF HALOALKANES IN
PURIFIED WATER USING HYDROCARBON SOLVENTS.

Solute	Solvent	V_w/V_o	$f_i \times 100$ Extraction Efficiency %	K_D Partition(a) Coefficient	References - Notes
CHCl ₃	n-Pentane	200	24	63	(8)
	"	100	43 (e)	73	(8)
	"	24	63 (2.3)	56	(30)
	"	20	82	91	
	"	10	82	46	(16) - (b)
	Iso-octane	10	78	35	(16) - (b)
	Methylcyclohexane	1	98	-	(15)
	"	5	93	-	(15)
	"	25	82	113	(15)
	n-Pentane	200	31	90	(8)
CHCl ₂ Br	"	100	50 (e)	100	(8) - (c)
	"	24	55.8 (0.5)	30	(31)
	"	20	89	161	
	"	10	89	81	(16) - (b)
	Iso-octane	10	85	57	(16) - (b)
	Methylcyclohexane	1	93	-	(15)
	"	5	92	-	(15)
	"	25	86	134	(15)
	n-Pentane	200	36	113	(8)
	"	100	57	133	(8) - (d)
CHClBr ₂	"	24	77.2 (0)	81	(31)
	"	20	84	105	
	"	10	91	-	(16) - (b)
	Iso-octane	10	88	73	(16) - (b)
	Methylcyclohexane	1	98	-	(15)
	"	5	97	-	(15)
	"	25	90	225	(15)
	n-Pentane	200	43	151	(8)
	"	100	63 (e)	170	(8) - (d)
	"	24	79.1 (0.6)	91	(31)
CHBr ₃	"	10	95	-	(16) - (b)

(continued)

TABLE 2. (continued)

Solute	Solvent	V_w/V_o	$f_i \times 100$ Extraction Efficiency %	K_D Partition Coefficient ^(a)	References - Notes
	Iso-octane	10	91	-	(16) - (b)
CCl ₄	n-Pentane	24	93.9 (0.6)	-	(31)
ClCH ₂ CH ₂ Cl	"	24	43.4 (0.8)	18	(31)

- (a) calculated from equation (3) except for f_i values above 0.90, where precision is poor;
 (b) average of values at analyte concentrations of 0.1-200 $\mu\text{g/L}$;
 (c) average of values at 1000 and 100 $\mu\text{g/L}$;
 (d) average of values at 1000, 100, 10 and 1 $\mu\text{g/L}$;
 (e) value in parenthesis is range of duplicate runs.

TABLE 3. EXTRACTION EFFICIENCIES OF HALOALKANES IN WASTEWATER USING N-PENTANE SOLVENT ($V_w/V_s = 100$) (10).

Solute	$f_i \times 100$ Extraction Efficiency (%)			K_D Partition Coefficient
	Value	S.D.	N	Value
CHCl ₃	79	21	21	376
CCl ₂ Br ₂	62	29	12	163
CCl ₄	71	14	14	244
ClCH ₂ CH ₂ Cl	65	14	18	186
CHCl=CCl ₂	69	22	21	222
Cl ₂ CHCH ₂ Cl	68	14	21	213
Cl ₂ CHCHCl ₂	97	25	21	-
ClCH ₂ CHClCH ₃	67	14	19	203

N = no. of determinations; S.D. = absolute standard deviation.

groups for the analysis of THMs in drinking water (26-30). The methods, which differ slightly from one laboratory to another, seem to be both precise and accurate. Olson and coworkers (28), for example, found the method to be superior in speed and comparable in precision to the purge and trap procedure (25). Relative standard deviations of less than 11% were obtained in all cases, with much of the data falling below 5%.

In an elaborate study in Great Britain reported by Croll (28), standard THM samples were analyzed using an LLE procedure. Both 5 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ standards in water, and a solvent sample of concentration equivalent to 100 $\mu\text{g/L}$ were analyzed by 15 laboratories. Intralaboratory tests of standard deviations at the 5 $\mu\text{g/L}$ level had a target of $\pm 1 \mu\text{g/L}$ for each THM, which was achieved by 13 of the 15 laboratories on the first round. The target at 100 $\mu\text{g/L}$ was $\pm 10\%$, which was achieved by 14 of the 15 laboratories.

EXTRACTION EFFICIENCIES OF HALOALKANES

Extraction efficiency is determined by the partition coefficient of the solute:solvent:water system K_D , which is itself a function of temperature; the volumetric ratio V_w/V_s ; and by matrix effects. In the absence of specific solute:water interactions, such as ionization, or complexation with other solutes, the effect of salts (ionic strength) is the principal effect expected from a change in matrix type.

The dependence of extraction efficiency on V_w/V_s and K_D is given by equation (3) and graphically shown in Figure 1.

Extraction efficiencies of some haloalkanes are shown in Table 2. Values of the partition coefficient K_D were calculated from these data using rearranged equation (15). The scatter in the values of K_D are not unexpected particularly since the data are from different laboratories. Richard and Junk (16) report reproducibility of $\pm 10\%$ in the values of extraction efficiencies. At a $f_i \times 100$ value of 85 this translates into a range of calculated K_D values from 33 to 143 at $V_w/V_s = 10$.

Table 3 shows extraction efficiencies for chloroform and other haloalkanes in a wastewater matrix (10). Presuming the V_w/V_s ratio used is 100:1, which is not absolutely clear from the paper (10), partition coefficients K_D may be calculated. The results, compared with the data in Table 2, suggest that extraction efficiencies in a wastewater matrix are higher than in purified water.

TABLE 4. RECOVERY OF VOLATILE ORGANOHALIDES BY MICROEXTRACTION^(a)

Compound	Concentration μg/L	Average Extraction Efficiency (Range)		
		Experiment 1	Experiment 2	Experiment 3
CHCl ₃	50	63.0 (2.3)	63.3 (0)	77.0 (1.9)
C ₂ H ₄ Cl ₂	45,000	43.4 (0.8)	43.6 (0.1)	68.0 (0.1)
CCl ₄	2.5	93.9 (0.6)	90.5 (4.0)	72.5 (2.6)
CHCl ₂ Br	10	55.8 (0.5)	56.5 (2.6)	65.1 (3.0)
CHClBr ₂	15	77.2 (0)	78.3 (1.8)	89.4 (0.3)
CHBr ₃	75	79.1 (0.5)	81.2 (2.0)	88.9 (1.8)
NaCl, Molarity		0	0.1	Saturated

(a) $V_w/V_s = 120/5 = 24$, n-pentane solvent. Data from Henderson (31)

TABLE 5. RECOVERY OF HALOALKANES AT 1000 μg/L FROM WATER CONTAINING DIFFERENT AMOUNTS OF METHANOL^a (8)

Haloalkane	Percent Recovery at			
	1% CH ₃ OH	5% CH ₃ OH	10% CH ₃ OH	20% CH ₃ OH
Chloroform	40	50	NM ^b	NM
Bromodichloromethane	47	47	48	41
Chlorodibromomethane	53	60	53	42
1,3-Dichloropropane	67	71	67	58
Bromoform	56	57	57	47

^a All extractions with pentane at $V_w/V_s = 100$

^b NM = not measured

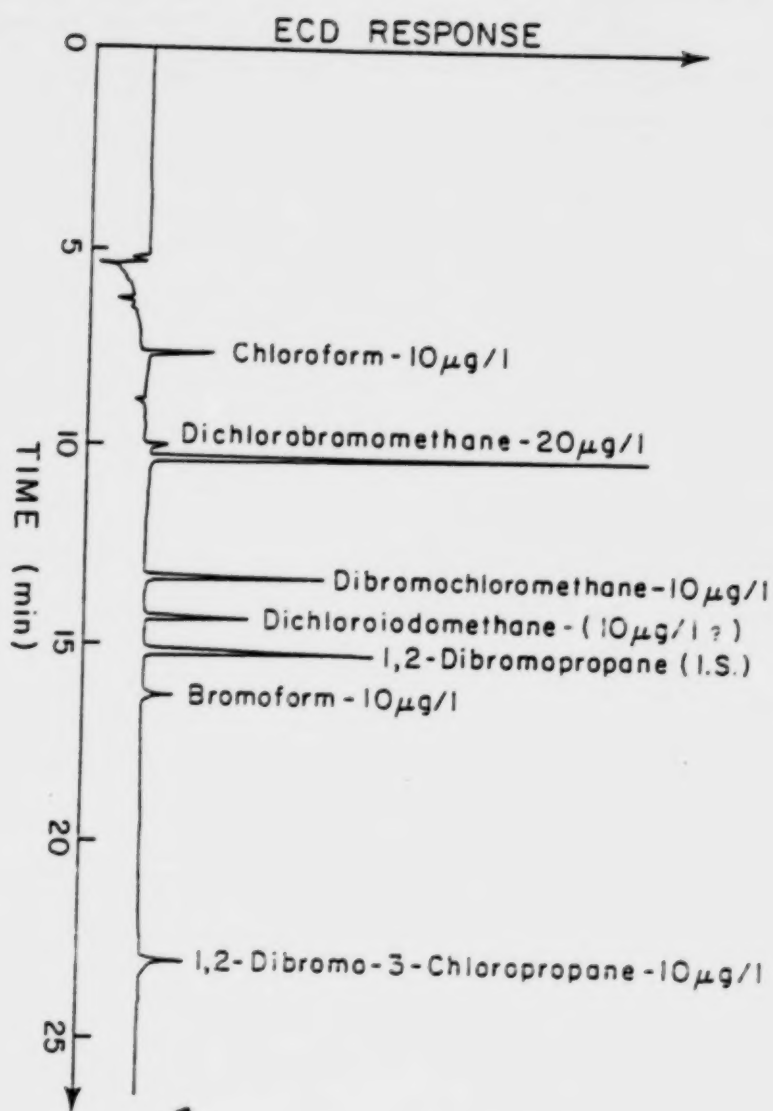


Figure 2. Typical chromatogram of THMs plus DBCP by LLE on SE-52 capillary column. (Taken from reference (30) by permission of Ann Arbor Science Publishers, Inc., Ann Arbor, MI.)

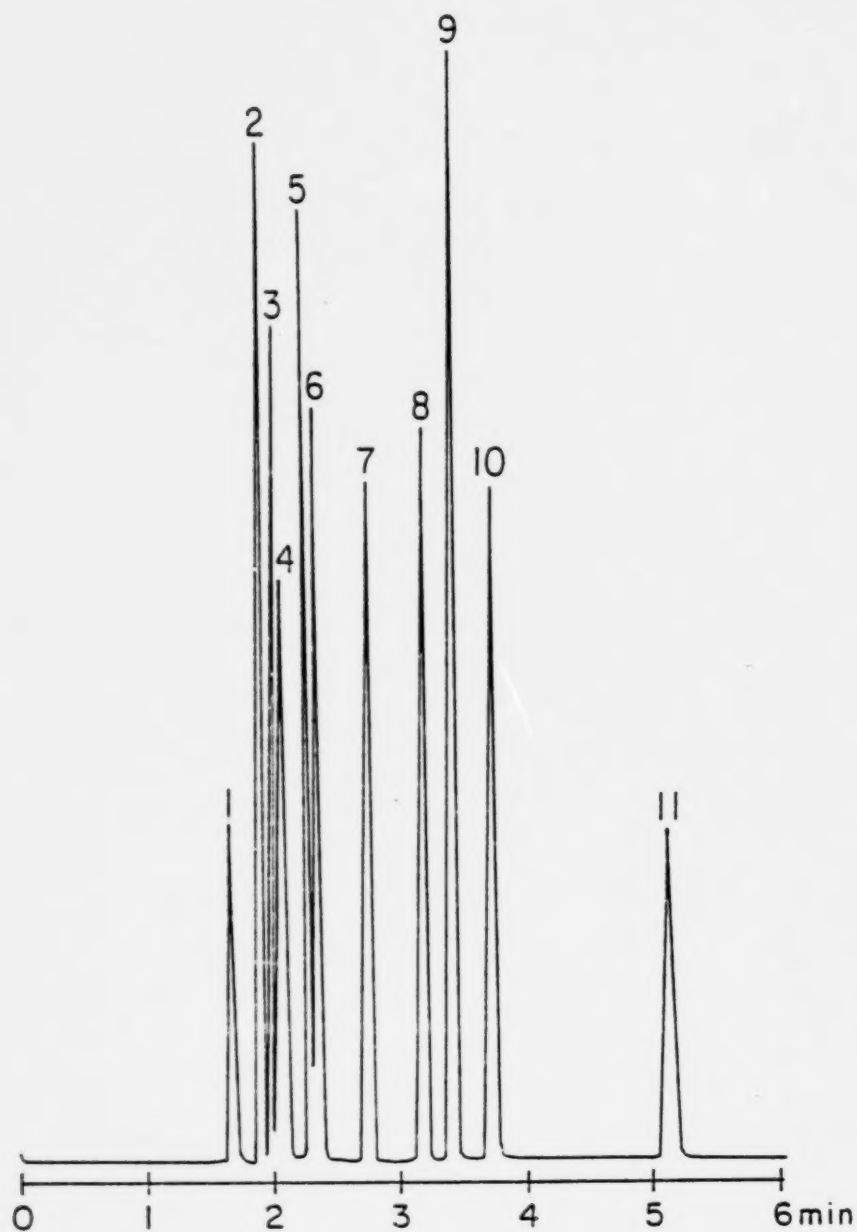


Figure 3. Capillary chromatogram of a standard mixture containing 11 organohalides. Stationary phase, SE-52; 33 m x 0.3 mm 1=CH₂Cl₂, 2=CHCl₃, 3=CH₃CCl₃, 4=CCl₄, 5=CHClCCl₂, 6=CHBrCl₂, 7=CBrCl₃, 8=CHBr₂Cl, 9=CCl₂CCl₂, 10=CHCl₂, 11=CHBr₃. (Taken from reference (19) with permission of Huthig Verlag, Heidelberg, Germany).

This effect is probably due to the higher total ionic strength in wastewaters. As previously noted, Mieux (15) suggested the addition of salt to increase the extraction efficiency when samples of low ionic strength were analyzed. Henderson (31) measured extraction efficiencies in purified water, 0.1 M NaCl and saturated NaCl solution. The results are shown in Table 4. With the exception of carbon tetrachloride which is anomalous, each compound shows an increase in extraction efficiency at the highest ionic strengths. It is significant that 100% efficiencies are not observed even from saturated salt solutions.

Richard and Junk (16) investigated the effect of added methanol on extraction efficiencies with the results shown in Table 5. Surprisingly, effects were not appreciable until 20% methanol was added. Richard and Junk concluded that extraction efficiencies be unaltered even when large quantities of some other water soluble components are present.

LLE FOR THE ANALYSIS OF OTHER MICROPOLLUTANTS IN WATER

The extension of the single-step LLE technique to the analysis of organic compounds in drinking water other than the THMs is also of interest. For this purpose, more efficient gas chromatography is often required. This may be accomplished to some extent using programmed temperature control of the GC column. This approach was used in the project described in this report and a preliminary publication has appeared (17). Details are given in Sections 5 and 6.

Optimum separation of complex mixtures of VOCs is obtained by the use of capillary column techniques. This approach was first used by Grob *et al.* who have pioneered the use of glass capillary columns for trace analysis (4).

Trussell and coworkers were among the first to use the LLE procedure combined with high performance capillary GC (CGC) for the analysis of THMs and other volatile organohalides in water. Figure 2 is a CGC trace of a VOC standard at 0.5 $\mu\text{g/L}$, which shows the separating power of this procedure. In this case the column was a 30 m x 0.25 mm SE-52 wall-coated column (30).

Eklund, Josefsson and Roos (19) also used a SE-52 coated (33 m x 0.3 mm) glass column with the results shown in Figure 3. In this case the column temperature was isothermal, whereas in Figure 2 a temperature program (40°C for six minutes, then 10°C/min to 130°C) was used.

ADVANTAGES AND DISADVANTAGES OF THE SINGLE-STEP LLE METHOD FOR THM AND VOC ANALYSIS

Advantages

1. Single-step LLE with GC analysis (LLE/GC) is a relatively simple procedure which requires a relatively low skill factor, perhaps as low as 2 on the EPA scale (32). Certainly a person of this level could carry out the procedure if supervised by a person of grade 3 or 4.
2. The LLE/GC method is rapid. Olson *et al.* (28) estimate that six samples per hour can be analyzed for THMs by the method as compared to 2.5 purge and trap analyses per hour. These frequencies will vary with sample load, number of blanks, purity of the sample (absence of non-THMs), and calibration standards, etc., but the relative speed of the LLE/GC method will prevail. Moreover, LLE/GC is amenable to semi-automation, *i.e.*, the use of automatic samplers for GC analysis after the extraction of a large group of samples.
3. The equipment required for LLE/GC analysis, a GC/EC is less expensive and more versatile than the purge and trap/GC apparatus. The former may also be used for pesticide analysis without modification.
4. Since calibration standards may be taken through the same procedure as samples, the need for a correction factor for incomplete recovery is avoided if matrix effects are small. As a result, accurate results are achieved even though recoveries are usually below 100%.
5. The precision of the LLE/GC method is generally within $\pm 20\%$ relative standard deviation. In favorable cases, *i.e.* simple matrices such as drinking water, precisions of $\pm 5\%$ are quite readily attainable.
6. With capillary GC techniques and with *n*-pentane as the solvent, the method may be extended to most of the C_1 and C_2 haloalkanes and many other organic species. With packed column technology the method is more limited, but may be applied for specific analytes if a two-column confirmatory GC procedure is used (1,24).
7. For many compounds of interest, *i.e.* most C_1 and C_2 haloalkanes, the LLE/GC procedure combined with ECD is sensitive below 1 $\mu\text{g/L}$. For THMs, which are currently regulated, sensitivity is excellent.

8. At least applied to drinking water analysis, the method appears to be insensitive to matrix effects such as variations in total dissolved solids and pH.

Disadvantages

1. Commercially available solvents usually contain impurities which interfere with the analysis of THMs and other VOCs. Some of these impurities may be removed by treatment with alumina (16) or by distillation (31,29); but the procedure is time consuming, tedious and dangerous, particularly in the hands of persons with low skill levels.
2. Solvents, once cleaned, can be easily contaminated by poorly controlled work environments. Whereas this is a general problem in organic trace analysis, the LLE method suffers more because of the affinity of solvents for organic vapors.
3. The LLE/GC procedure is more susceptible to sample interferences because of the sensitivity of the ECD vis a vis the Hall detector used in the purge and trap procedure approved by EPA (1).
4. The confirmation of compounds by GC/MS is difficult if a LLE procedure is used for preconcentration. For example, if a solute is present at 100 µg/L, extraction of 10 mL with 1 mL of solvent with 100% efficiency will yield 1 µg of solute in the 1 mL of solvent. Only 1-3 µL of this can be injected into the GC/MS, so only 1-3 ng of solute is available for confirmation. While this quantity is sufficient for detection by selected ion monitoring or by negative ion/chemical ionization spectroscopy (30), it is generally not enough for obtaining a whole electron impact spectrum by GC/MS. So, larger quantities are needed for GC/MS confirmation, requiring a modified LLE procedure.
5. While the LLE/GC procedure can be extended to compounds other than the THMs, the procedure has not been well tested and difficulties are apparent. Thus, some compounds (e.g. 1,2-dichloroethane) have low electron capture cross sections and (therefore), high limits of detection. In addition, complex mixtures will require the use of capillary column chromatography, thus eliminating the advantage of simplicity (advantage 1 above).
6. The LLE method is subject to salt effects; thus, it cannot be used for brackish or sea waters without appropriate corrections. Even in wastewater samples, standardization is a similar matrix is needed to eliminate variations in extraction efficiencies; at least for work of the highest precision.

The work described in this report actually began before a majority of the papers described in this Section appeared in the literature. Thus, the work here, partially described at scientific meetings and in proceedings, was contemporary with other works which used and extended the LLE/GC method. The following sections describe our work on the optimization of the method in more detail than it has been described before. In addition, new work is described which compares the LLE/GC method with a purge and trap procedure using samples from actual drinking water systems.

SECTION 4

EXPERIMENTAL

MATERIALS

Reagent Water

Reagent water was prepared by laboratory treatment of either tap water, or, in some cases, bottled water. The most common procedure was to deionize the water with a commercially available mixed-bed resin cartridge, followed by filtration with activated carbon. A 0.45 μ filter was usually the final step, but at times there was a final polish using a slow helium purge. Commercial systems for preparation of very pure water are available from Millipore, Culligan and other manufacturers.

Solvents

Several commercial sources of *n*-pentane were used including Fisher Scientific, Mallinckrodt, Burdick and Jackson, and Baker. Other solvents such as hexane, methylcyclohexane and isooctane were obtained from the same suppliers. In general, *n*-pentane from commercial suppliers was found to contain traces ($\mu\text{g/L}$) of impurities which responded to the ECD. These most often eluted at or before the retention time of chloroform. Simple distillation of the solvent usually reduced the level of these impurities providing a center cut was taken. Distillation from freshly cut sodium chips was the preferred method, but it was extremely difficult to prepare *n*-pentane, from which chloroform interference is absent. In addition to distillation, *n*-pentane and other hydrocarbon solvents may be purified by passage through a column of basic alumina (16). The column used was 15-in. x 0.75-in. i.d., and was sufficient to purify several hundred mL of solvent. No preparation of the alumina was required. The pentane was poured through the column, with no pressure applied; a flowrate of about 3 mL/min. was achieved with gravity feed. All hydrocarbon solvents easily pick up contaminants from laboratory atmosphere; therefore, after purification, solvents were stored in tight glass containers, preferably in an explosion-proof refrigerator. Care was also taken to avoid the use of polymer-lined caps which might contaminate solvents stored in glass bottles.

Sample Bottles

Three types of sample vials were used in this work. The original method used a 125-mL septum bottle with an aluminum crimp top. Smaller, 40 or 25 mL, vials with screw caps were later used. In all cases, a silicone rubber septum liner was used with a Teflon face toward the water sample (1). Sample vials and Teflon-lined septa may be obtained from several suppliers including Supelco, Pierce, and Applied Sciences.

Pure Reference Standards

Pure compounds were purchased from several suppliers and were the best grade available. In most cases, the compounds were used as received unless a GC survey showed the presence of copious impurities. In this case, the compound was distilled carefully to an acceptable level of purity.

Chromatographic Columns and Gases

Except for capillary columns, GC columns were generally packed in the laboratory. In some cases the liquid phase was coated on the stationary phase by the usual procedure. A solution of the liquid phase in a non-interfering volatile solvent was stirred with stationary phase in a rotary evaporator while removing the solvent under reduced pressure. The column was packed by gentle vibration and conditioned above the temperature it was to be used. Glass capillary columns were purchased from J & W Scientific or Supelco. Fused silica columns came from Hewlett-Packard Instruments or J & W Scientific.

Chromatography gases were the highest quality available. Molecular sieve filters were used routinely, particularly to protect EC detectors.

PROCEDURES

Glassware Cleaning

All glassware was washed with detergent, rinsed with deionized water, then with pure water. In some cases, a final acetone rinse was used, but generally the glassware was dried several hours in a 150-180°C oven. Tops of the vessel were covered with aluminum foil for storage.

Sampling

Water samples were obtained without headspace, thereby preventing loss of volatile compounds (1). The rigorously

cleaned sample bottles were filled just to overflowing with sample, and a septum (Supelco 2-3276) and cap were placed on the bottle with the Teflon (shiny) side against the sample. Samples were maintained in an ice chest or cold room until the extraction step, at which time they were warmed to room temperature. Analysis was conducted as soon after extraction as possible.

Buffer-Quench Solution

A solution of phosphate buffer and sodium sulfite was usually added to each bottle just prior to sampling. The buffer assures that the sample will be analyzed at a pH of 6.5, while the sulfite quenches residual chlorine. The buffer-quench solution was prepared by mixing four volumes of 1.0 M NaH_2PO_4 /0.1 M Na_2SO_3 and six volumes of 1.0 M Na_2HPO_4 ; 0.25 or 1 mL was added to each 25- or 120-mL bottle just prior to sampling. Bottles containing standards and blanks also had this solution added prior to separation.

Standards

Stock solutions of the organohalides were prepared gravimetrically in nanograde methanol according to the EPA method (1). With storage at 4°C, these stock solutions did not change in concentration for at least four weeks.

Two secondary dilution mixtures were prepared in methanol from the stock solutions. The first, the quality check standard mixture, contained 5.0 ng/ μL of each compound, so that a 10- μL injection into 25 mL of reagent water yielded a solution containing 2.0 $\mu\text{g/L}$ of each compound. The second, called the calibration standard mixture, contained a quantity of each compound so that a 10- μL injection into 25 mL of reagent water generated a calibration standard very similar ($\pm 10\%$) to the unknown. The aqueous calibration standards were not stable and were made up fresh for each sample set.

Internal Standard in n-Pentane

The internal standard (IS) usually used in this procedure was 1,2-dibromoethane, although others were used occasionally (see below). A 200 $\mu\text{g/L}$ solution of the internal standard in pentane was prepared and stored at ambient temperature in the dark in a volumetric flask with a ground-glass stopper. A quantity of this mixture sufficient for several runs was prepared in advance, and was chromatographed prior to each use as a check against contaminants. No significant degradation was observed over a period of 4-6 weeks. The pentane was checked by GC/ECD prior to making up this solution. If contaminants were present,

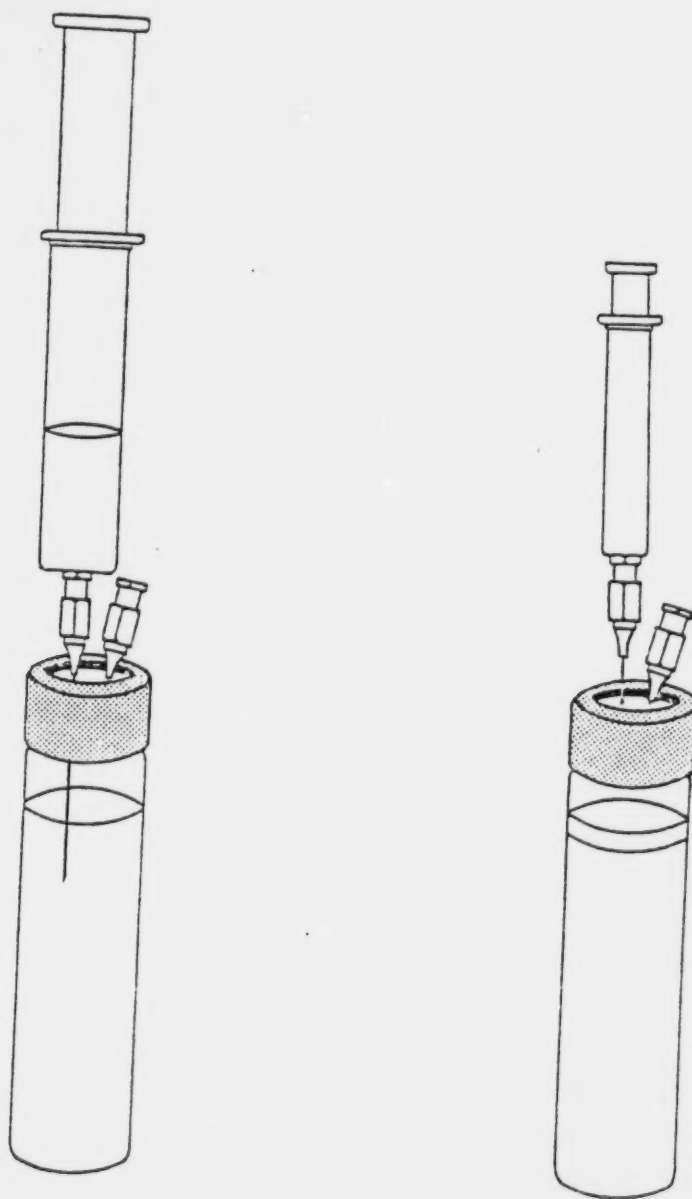


Figure 4. Procedure for removal of water (left) and addition of hydrocarbon (right) prior to LLE/GC.

they were removed by distillation over sodium or by passage through an alumina column (see above).

Extraction: The Original Method

This method was described in detail before, (14) and was not a part of the current project. In brief, the method utilized a 125-mL headspace-free sample taken according to EPA specifications (1). A 5-mL sample of water was removed from the bottle with a syringe, and 5 mL (or later 3 mL) of *n*-pentane added to the bottle with a second syringe. In the original method described by Henderson *et al.* (14), the water was removed and pentane added simultaneously, but this manipulation is not necessarily required. Nor is it necessary to replace the water with an equal volume of pentane, since headspace has not been found to be a detrimental factor after addition of solvent.

Extraction: The Modified Method

Solvent Addition and Extraction--

The extraction procedure involved two steps: water removal, and pentane addition. To allow a headspace for addition and mixing of the solvent, 5 mL of water was removed from each sample through the septum with a glass syringe (Figure 4). A second needle allowed air to replace the water. The syringe was first flushed with reagent water, so that the needle contained no air. This enabled the water to be slowly removed with accuracy, without the complication of bubbles in the syringe during the process.

Pentane was added to the sample with the bottle upright, and with the second needle still in the bottle. The needle point was kept well above the water surface, so that air was expelled as the pentane/internal standard solution was added (Figure 4). After this addition, the syringe and needles were removed, and the bottle was shaken vigorously by hand for one minute or with a laboratory vortex shaker (Sybron/Thermolyne Model M16715) for 30 seconds. Following this, the bottle was inverted and allowed to stand for at least one minute, enabling the phases to separate. The bottle was kept with the cap down, except when the pentane was being sampled for chromatography.

Extraction: The Modified 120:0.5 Method

The extraction procedure in the third-generation LLE method involved the use of a 100- or 120-mL bottle depending on availability. Bottles were spiked with a quenching agent as before and with 5 g of sodium chloride (analytical reagent grade). One mL of water was removed from the sample bottle as

described in the previous section. Next, 0.5 mL of pentane was added slowly while the sample bottle was sitting in a small ultrasonic bath (Heat Systems Ultrasonics, Inc., Model D-50). The pentane dispersed into fine droplets immediately on being injected into the water. The bottle was then mixed for one minute on a vortex shaker and allowed to sit until the two layers separated. The latter process was facilitated by the addition of salt as noted above.

Packed-Column Gas Chromatography

Several packed columns have been found to resolve THMs including squalane, SP-2100, SP-1000 and porous polymers. The column used routinely was 10% squalene on 80/100 mesh Chromasorb W/AW. The column was glass, 9 ft. x 2 mm i.d. Chromatographic conditions were as follows: oven, 68°C; injection port, 100°C; ⁶³Ni detector, 350°C; argon-methane (90:10) carrier flow, 20 mL/minutes; amount of sample injected, 2 µL.

The detector was a linearized ⁶³Ni ECD. An electronic integrator was used for quantification of compounds.

A second chromatographic column was used for confirmation purposes and to resolve other halogenated organics. This column was also 9 ft. x 2 mm i.d., and contained a mixed phase 6% OV-11 and 4% SP-2100 on 100/120 mesh Supelcoport. The column was programmed from 45°C after 12 minutes, at 1°/minutes, to 75°C. With this program, the column resolved THMs and six other organohalides: carbon tetrachloride, 1,1,1-trichloroethane, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene and dichlorodiodomethane. The last compound, bromoform, eluted at 39 minutes under these conditions.

Capillary Gas Chromatography

One column used in this work was a 60-m x 0.25-mm i.d. glass column with SE-54 wall coating (Supelco). Conditions for GC/FD chromatography on the Hewlett-Packard 5840 were as follows: initial temperature: 0°C; purge delay for splitless injection: 0.5 minutes; septum purge 4 mL/minutes; inlet purge: 70 mL/minutes; temperature program: hold at 0°C 1-3 minutes, then to 120°C at 3°/minutes, stop at 40 minutes; linear helium velocity: 31 cm/second at 0°C; helium makeup: 40 mL/minutes. Conditions for ECD were the same except that 50 mL/minutes of argon/methane makeup gas was used. Essentially the same conditions were used with 30 m x 0.25 mm i.d. fused silica capillary WCOT columns with SE-54 liquid phase, two of which were used in later stages of the project.

Purge and Trap Analysis

The Hewlett-Packard Model 7675A Purge and Trap Module was used essentially as prescribed by the manufacturer. The instrument was coupled directly to the HP 5840A gas chromatograph. Five-mL samples were purged for 10 minutes at helium flow rate of 40 mL/minutes. Trap desorption was at 250° for five minutes, followed by a purge vent at 300°C. The glass column was 6 ft. x 2 mm i.d. with 0.2% Carbowax 1500 on 80/100 mesh Carbopak C (Supelco). For organohalides the initial temperature during trap desorption was 60°C. At start of the program, the temperature was held at 60° for three minutes, then raised to 130°C at 8°C/minute. The carrier gas was argon/methane at 35 mL/minute and the detector was the ⁶³Ni EC. For aromatic hydrocarbons, the same column was used with the following temperature program: 130°C, three minutes; 15°C/minute to 160°C, hold to 45 minutes. The carrier gas was helium with a flow of 35 mL/minute. The internal standard was 1,2-dibromoethane for ECD, and n-nonane for hydrocarbon analysis by FD.

SECTION 5

RESULTS AND DISCUSSION

EXTRACTION EFFICIENCIES

Following an LLE experiment, the fractional extraction efficiency f_i , is given by the following definition:

$$f_i = \frac{\text{mass of } i \text{ in solvent after extraction}}{\text{mass of } i \text{ in solvent and water}} = \frac{m_i^p}{m_i^w + m_i^p}$$

To determine f_i , one may spike a known quantity of the solute i into water (m_i^w), carry out the extraction, and then determine m_i^p , the mass of solute in the pentane layer. Assuming $m_i^T = m_i^w + m_i^p$, E may be calculated. To determine m_i , the usual GC calibration procedure must be supplanted with a procedure in which a pentane solution of known concentration is used to determine GC response factors. These response factors are then used to convert GC peak areas into masses of solutes in the pentane layer after extraction. The appropriate steps and equations are as follows:

1. Prepare n-pentane standard (25 mL) from methanol primary standard. Concentration of solute i is $[i]_0$.
2. GC n-pentane standard and determine area count for solute A . Calculate concentration response factor for solute i (if desired)

$$R_i = A_i^O / [i]_0$$

3. Prepare water standard (25 mL) of same concentration as n-pentane standard, $[i]_T = [i]_0$ extract with 1.0 mL n-pentane to equilibrium.

4. GC n-pentane layer under same conditions as above. Determine area count of solute i , A . Calculate concentration of i in pentane layer, $[i]_p$.

TABLE 6 . LLE EXTRACTION EFFICIENCIES (20:1) IN
ORGANIC FREE WATER^a

Compound	Blank ^b ($\mu\text{g/L}$)	Spike Concentration ($\mu\text{g/L}$)	N ^c	Average Efficiency ^d (%)
Chloroform	0.4	19	5	77 $\pm$ 5
		90	4	82 $\pm$ 2
		Weighted Average		79 $\pm$ 4
1,1,1-Trichloro- ethane	0.09	10	5	92 $\pm$ 7
		49	4	95 $\pm$ 2
		Weighted Average		93 $\pm$ 5
Carbon Tetra- chloride	0.05	10	5	93 $\pm$ 7
		50	4	89 $\pm$ 2
		Weighted Average		91 $\pm$ 5
1,2-Dichloroethane		400	5	73 $\pm$ 4
		1890	4	69 $\pm$ 3
		Weighted Average		71 $\pm$ 4
Trichloroethylene	0.04	16	5	88 $\pm$ 17
		71	4	90 $\pm$ 2
		Weighted Average		89 $\pm$ 13
Bromodichloro- methane		20	5	80 $\pm$ 6
		90	4	84 $\pm$ 2
		Weighted Average		82 $\pm$ 5
Tetrachloro- ethylene	0.3	23	5	95 $\pm$ 10
		106	4	89 $\pm$ 1.5
		Weighted Average		92 $\pm$ 8
Dibromochloro- methane		21	5	83 $\pm$ 8
		98	4	88 $\pm$ 2
		Weighted Average		85 $\pm$ 6
Bromoform		12	5	89 $\pm$ 10
		58	4	88 $\pm$ 2
		Weighted Average		89 $\pm$ 8

- ^a Determined on the HP 5840A with the mixed phase column vs.
pentane calibration standards. Calculated without internal std.
^b "Organic free" water, pentane, & internal std. contaminant level.
^c Number of replicate extractions per spike level.
^d Standard deviation of individual efficiency data point, not
standard error.

$$[i]_p = A_i^p / R = [i]_o \cdot A_i^p / A_i^o$$

5. Since

$$f_i = m_i^p / m_i^T = \frac{[i]_p \cdot V_p}{[i]_T \cdot V_w} = \frac{[i]_p \cdot V_p}{[i]_o \cdot V_w}$$

then it follows that f_i may be calculated directly from the area ratios corrected for the volumetric factor, i.e.

$$f_i = (A_i^p / A_i^o) \cdot (V_p / V_w) = (A_i^p / A_i^o) \cdot 1/20$$

If the blank level of solute i is not negligible, then the area A must be corrected (see below). In the present case, the blank levels were also negligible.

Results--

In one series of experiments "reagent" water originally containing 0.4 $\mu\text{g/L}$ chloroform, 0.09 $\mu\text{g/L}$ 1,1,1-trichloroethane, 0.1 $\mu\text{g/L}$ carbon tetrachloride, 0.04 $\mu\text{g/L}$ trichloroethylene and 0.3 $\mu\text{g/L}$ tetrachloroethylene was spiked with nine VOCs at various concentrations (Table 6).

From four to five replicate pentane extractions of each spike concentration were analyzed relative to pentane calibration standards on the HP 5840A with the mixed phase column (6% OV-11 and 4% SP-2100). A 12-minute isothermal (40°C) run followed by a 1°C/minute program up to 80°C was used. The results are listed in Table 6.

Since the blank concentrations are negligible compared to the spike concentrations, the extraction efficiencies are given directly by the spike recoveries. The average efficiencies ranged from 69% for 1,2-dichloroethane to 95% for tetrachloroethylene and 1,1,1-trichloroethane. The former compound has a low response factor, is very close to the carbon tetrachloride peak, and is difficult to integrate accurately.

Table 6 shows no differences in extraction efficiencies at different concentrations. Assuming this is the case, weighted average efficiencies were calculated for each compound. Each average efficiency was weighted in the final average by the number of extractions involved and inversely proportional to its variance. The resulting weighted averages ranged from 71% for 1,2-dichloroethane to 93% for 1,1,1-trichloroethane. The median weighted average extraction efficiency for all nine compounds was

TABLE 7. LLE EXTRACTION EFFICIENCIES (20:1) IN ORGANIC FREE WATER^a

Compound	Spike Concentration ($\mu\text{g/L}$)	N ^b	Average Efficiency ^c (%)
Chloroform	100	4	71 $\pm$ 4
	200	2	73 $\pm$ 1
		Weighted Average	72 $\pm$ 4
1,1,1-Trichloroethane	45	4	84 $\pm$ 4
	90	2	93 $\pm$ 2
		Weighted Average	86 $\pm$ 4
Carbon tetrachloride	61	4	83 $\pm$ 8
	120	2	95 $\pm$ 2
		Weighted Average	89 $\pm$ 7
1,2-Dichloroethane	890	4	54 $\pm$ 3
	1800	2	59 $\pm$ 2
		Weighted Average	56 $\pm$ 3
Trichloroethylene	49	4	84 $\pm$ 4
	98	2	91 $\pm$ 2
		Weighted Average	86 $\pm$ 4
Bromodichloromethane	100	4	71 $\pm$ 6
	210	2	77 $\pm$ 2
		Weighted Average	73 $\pm$ 5
Tetrachloroethylene	57	4	85 $\pm$ 5
	110	2	93 $\pm$ 1
		Weighted Average	87 $\pm$ 4
Dibromochloromethane	110	4	74 $\pm$ 6
	220	2	77.8 $\pm$ 0.3
		Weighted Average	75 $\pm$ 5
Bromoform	54	4	73 $\pm$ 4
	110	2	85 $\pm$ 4
		Weighted Average	77 $\pm$ 4

^a Determined on the HP 5840A with the mixed phase column vs. pentane calibration standards.

^b Number of replicate extractions per spike level.

^c Standard deviation of individual efficiency data point, not standard error.

86% with the four THM efficiencies at 79 to 88%.

Additional experiments were carried out to verify and augment the extraction efficiencies obtained in reagent water. The water, which originally contained less than 0.1 $\mu\text{g/L}$ of any of the nine compounds, was spiked with nominal 100 and 200 $\mu\text{g/L}$ concentrations of the THMs. (Bromoform was 50 and 100 $\mu\text{g/L}$) and 50 and 100 $\mu\text{g/L}$ of the non-THMs (1,2-Dichloroethane was 890 and 1800 $\mu\text{g/L}$). Duplicate or quadruplicate extractions were then analyzed relative to pentane standards with the procedure mentioned previously. The results are given in Table 7. These weighted averages agreed with the previous ones to within the assigned errors except for the erratic 1,2-dichloroethane results. However, the average efficiencies shown in Table 7 as a group are lower than the previous ones.

In an attempt to determine the extraction efficiencies of the nine compounds from an actual drinking water sample, Denton tap water was spiked at the same concentrations as was the reagent water. The tap water before spiking contained 22 to 48 $\mu\text{g/L}$ chloroform, 0.1 to 0.3 $\mu\text{g/L}$ carbon tetrachloride, 20 to 33 $\mu\text{g/L}$ bromodichloromethane, 0.4 to 0.5 $\mu\text{g/L}$ tetrachloroethylene, 15 to 22 dibromochloromethane, and 1.6 to 3.1 $\mu\text{g/L}$ bromoform. Its pH was 7 to 7.6, and its conductivity was 435 to 460 micromhos/cm. For each spike level, three to four replicate extractions were performed; the pentane extracts were analyzed vs. pentane calibration solutions using the mixed phase column and the same procedure used for the reagent water series.

The extraction efficiencies for those compounds which have negligible blank concentrations relative to the spike concentrations may be calculated directly by the equations given on page 30. For other compounds, namely the THMs, the data interpretation is more complicated since the blank concentrations inherently include the unknown extraction efficiencies which are being sought. The extraction efficiencies of the THMs in Denton tap water are unlikely to be 100%, and so the experimental blank concentrations will be lower than the true concentrations.

Therefore, some assumption regarding the extraction efficiencies of the blank must be made prior to determination of the unknown extraction efficiencies of the spiked samples. A reasonable assumption is that the blank and spiked samples have the same extraction efficiencies. Assume that the blank was run under the same conditions as the water (spiked) sample; with area count A_i . Then the concentration of i in the blank is given by:

TABLE 8. LLE EXTRACTION EFFICIENCIES (20:1) OF NINE VOLATILE HALIDES FROM DENTON TAP WATER^a

Compound	Blank ^b (µg/L)	Spike Concentration (µg/L)	N ^c	Average Efficiency (%)
Chloroform	22	19	4	72 ± 2
	48	90	3	71.0 ± 0.4
			Weighted Average ^d	72 ± 2
1,1,1-Trichloro- ethane		10	4	80.3 ± 0.6
		49	3	91.4 ± 0.6
			Weighted Average	85.8 ± 0.6
Carbon tetra- chloride	0.1	10	4	83.6 ± 0.5
	0.3	50	3	99.2 ± 0.9
			Weighted Average	90.3 ± 0.6
1,2-Dichloro- ethane		400	4	62 ± 3
		1890	3	73 ± 1
			Weighted Average	66 ± 2
Trichloro- ethylene		16	4	80.2 ± 0.8
		71	3	94.0 ± 0.5
			Weighted Average	86.1 ± 0.7
Bromodichloro- methane	20	20	4	63 ± 2
	33	90	3	75.5 ± 0.9
			Weighted Average	68 ± 2
Tetrachloro- ethylene	0.5	23	4	84 ± 4
	0.4	105	3	102 ± 1
			Weighted Average	90 ± 3
Dibromochloro- methane	15	21	4	61 ± 4
	22	98	3	84 ± 2
			Weighted Average	72 ± 3
Bromoform	1.6	12	4	70 ± 5
	3.1	58	3	90 ± 2
			Weighted Average	78 ± 4

^aDetermined on the HP 5840A with the mixed phase column vs. pentane standards.

^bUnpurged tap water with pH of 7.0 to 7.6 and conductivity of 435 to 460 micromhos/cm.

^cNumber of replicate extractions at each spike level.

^dEach individual mean was weighted inversely proportional to its variance.

TABLE 9. LLE EXTRACTION EFFICIENCIES (20:1) OF NINE
VOLATILE HALIDES FROM DENTON TAP WATER^a

Compound	Blank ^b ($\mu\text{g/L}$)	Spike Concentration ($\mu\text{g/L}$)	N ^c	Average Efficiency (%)
Chloroform	52	100	3	68.8 $\pm$ 0.8
1,1,1-Trichloro- ethane		45	3	88 $\pm$ 1
Carbon Tetra- chloride	0.2	61	3	87.9 $\pm$ 0.8
1,2-Dichloro- ethane		890	3	55 $\pm$ 2
Trichloro- ethylene		49	3	85.4 $\pm$ 0.7
Bromodichloro- methane	36	100	3	74.5 $\pm$ 0.8
Tetrachloro- ethylene	0.2	57	3	85 $\pm$ 2
Dibromochloro- methane	29	110	3	76.3 $\pm$ 0.7
Bromoform	4.1	54	3	79 $\pm$ 2

^aDetermined on the HP 5840A with the mixed phase column vs. pentane standards.

^bUnpurged tap water with pH of 7.6 and conductivity of 405 micromhos/cm.

^cNumber of replicate extractions at each spike level.

TABLE 10. PARTITION COEFFICIENTS FOR VOCs IN WATER:
N-PENTANE ($V_w/V_s = 20$)

Compound	Concentration Range ($\mu\text{g/L}$)	Matrix	K_D
CHCl_3	100, 200	RW	54)
	100	DTW	44)
CHCl_2Br	100	RW	63)
		DTW	60)
CHClBr_2	110	RW	71)
		DTW	63)
CHBr_3	54	RW	67)
		DTW	75)
CCl_4	61	RW	313)
		DTW	147)
MC	45	RW	180)
		DTW	147)
TCE	49	RW	162)
		DTW	113)
PCE	57	RW	230)
		DTW	113)
DCE	890	RW	26)
		DTW	24)

RW = Reagent water; DTW = Denton tap water

$$\begin{aligned} \text{Then } [i]_b &= [i]_o \cdot A_i / A_i \\ \text{and } [i]_p &= [i]_o \cdot A_i / A_i - [i]_o \cdot A_i / A_i \\ E &= (A_i / A_i) - (A_i / A_i) \end{aligned}$$

20

Again, A_i , A_i and A_i are area counts for equal injection volumes of component i in the pentane layer after extraction of water spike (A_i); the pentane layer after extraction of the blank water (A_i), and in the pentane calibration standard (A_i) respectively.

The results of the calculated extraction efficiencies for all nine compounds are presented in Table 8. The efficiencies for the compounds with negligible blanks range from 62% for 1,2-dichloroethane to 102% for tetrachloroethylene. The weighted means for these compounds ranged from 68% for Bromodichloromethane to 90% for tetrachloroethylene with a median of 79%. The average extraction efficiencies for the THMs ranged from 61% for dibromochloromethane to 90% for bromoform. The weighted averages ranged from 68% for bromodichloromethane to 78% for bromoform with a median of 79%.

Additional experiments were carried out to confirm these results using Denton tap water originally containing 52 $\mu\text{g/L}$ chloroform, 36 $\mu\text{g/L}$ bromodichloromethane, 29 $\mu\text{g/L}$ dibromochloromethane, and 4.1 $\mu\text{g/L}$ bromoform. Spikes of a nominal 50 $\mu\text{g/L}$ for non-THMs and bromoform and 100 $\mu\text{g/L}$ for other THMs were used. 1,2-Dichloroethane was spiked at 890 $\mu\text{g/L}$. The spiked aqueous solutions were extracted in triplicate and analyzed vs. pentane standards using the procedure described previously. The results are shown in Table 9. The average extraction efficiencies agreed well with the previous weighted averages except for tetrachloroethylene, ($85 \pm 2\%$) which appears to be too high ($90 \pm 3\%$) in the previous work, and for bromoform ($79 \pm 2\%$ vs. $78 \pm 4\%$).

Calculation of Partition Coefficients

Partition coefficient K_D may be calculated from the data in Tables 6-9 for the nine VOCs. Presuming the data taken later in the study are more accurate, K_D values are calculated from Table 7 (purified water) and Table 9 (Denton tap water). The results are given in Table 10.

With the exception of CCl_4 , which is anomalous, the extraction efficiencies appear to be slightly higher in Denton tap water than in reagent water. In many cases, however, the

TABLE 11. EFFECT OF pH AND IONIC STRENGTH (μ) UPON
PENTANE LLE EFFICIENCY OF CHLOROFORM IN
WATER

μ	pH			
	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>
200 $\mu\text{g/L}^*$				
0.1	2.64 $\pm$.11	2.58 $\pm$.01	2.51 $\pm$.08	2.66 $\pm$.05
0.01	2.53 $\pm$.10	2.44 $\pm$.05	2.44 $\pm$.0	2.53 $\pm$.03
0.001	2.08 $\pm$.06	2.12 $\pm$.20	1.83 $\pm$.18	2.06 $\pm$.04

*Reported as 10^6 Integrator Counts

40 $\mu\text{g/L}^*$				
0.1	4.04 $\pm$.17	3.41 $\pm$.16	3.88 $\pm$.41	3.87 $\pm$.15
0.01	3.53 $\pm$.39	4.03 $\pm$.16	3.96 $\pm$.17	3.88 $\pm$.08
0.001	3.98 $\pm$.18	3.38 $\pm$.08	3.37 $\pm$.09	4.14 $\pm$.06

*Reported as 10^5 Integrator Counts

8 $\mu\text{g/L}^*$				
0.1	6.16 $\pm$.63	7.21 $\pm$.10	5.76 $\pm$.20	6.28 $\pm$.31
0.01	7.93 $\pm$.50	7.77 $\pm$.45	7.76 $\pm$.04	7.91 $\pm$.52
0.001	7.85 $\pm$.28	8.40 $\pm$.33	7.87 $\pm$.18	7.60 $\pm$.59

*Reported as 10^4 Integrator Counts

TABLE 12. EFFECT OF pH AND IONIC STRENGTH (μ) UPON
PENTANE LLE EFFICIENCY OF BROMODICHLORO-
METHANE IN WATER

μ	pH				
	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	
200 $\mu\text{g/L}^*$					
0.1	9.68 $\pm$.33	9.42 $\pm$.02	9.20 $\pm$.23	9.70 $\pm$.14	
0.01	9.40 $\pm$.35	9.15 $\pm$.16	9.16 $\pm$.0	9.41 $\pm$.09	
0.001	7.98 $\pm$.21	8.07 $\pm$.66	7.12 $\pm$.62	7.91 $\pm$.12	
*Reported as 10^6 Integrator Counts					
40 $\mu\text{g/L}^*$					
0.1	1.752 $\pm$.064	1.514 $\pm$.066	1.302 $\pm$.160	1.682 $\pm$.058	
0.01	1.572 $\pm$.020	1.770 $\pm$.064	1.734 $\pm$.069	1.697 $\pm$.040	
0.001	1.746 $\pm$.076	1.486 $\pm$.026	1.478 $\pm$.030	1.798 $\pm$.020	
*Reported as 10^6 Integrator Counts					
8 $\mu\text{g/L}^*$					
0.1	2.70 $\pm$.24	3.07 $\pm$.13	2.53 $\pm$.01	2.73 $\pm$.11	
0.01	3.38 $\pm$.17	3.37 $\pm$.14	3.25 $\pm$.01	3.33 $\pm$.17	
0.001	3.34 $\pm$.11	3.53 $\pm$.10	3.39 $\pm$.02	3.24 $\pm$.18	
*Reported as 10^5 Integrator Counts					

TABLE 13. EFFECT OF pH AND IONIC STRENGTH (μ) UPON
PENTANE LLE EFFICIENCY OF DIBROMOCHLOROMETHANE
IN WATER

μ	pH				
	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	
200 $\mu\text{g/L}^*$					
0.1	8.94 $\pm$.35	8.68 $\pm$ 0	8.47 $\pm$.22	8.96 $\pm$.18	
0.01	8.70 $\pm$.37	8.44 $\pm$.13	8.47 $\pm$.02	8.70 $\pm$.10	
0.001	7.30 $\pm$.20	7.40 $\pm$.63	6.50 $\pm$.60	7.28 $\pm$.14	
*Reported as 10^6 Integrator Counts					
40 $\mu\text{g/L}^*$					
0.1	1.52 $\pm$.05	1.30 $\pm$.06	1.11 $\pm$.14	1.45 $\pm$.05	
0.01	1.35 $\pm$.05	1.54 $\pm$.06	1.50 $\pm$.06	1.48 $\pm$.03	
0.001	1.51 $\pm$.07	1.28 $\pm$.02	1.26 $\pm$.03	1.56 $\pm$.01	
*Reported as 10^6 Integrator Counts					
8 $\mu\text{g/L}^*$					
0.1	2.05 $\pm$.19	2.35 $\pm$.02	1.90 $\pm$.0	2.06 $\pm$.08	
0.01	2.63 $\pm$.14	2.62 $\pm$.11	2.55 $\pm$.01	2.60 $\pm$.14	
0.001	2.61 $\pm$.11	2.76 $\pm$.04	2.64 $\pm$.0	2.51 $\pm$.14	
*Reported as 10^5 Integrator Counts					

TABLE 14. EFFECT OF pH AND IONIC STRENGTH (μ) UPON
PENTANE LLE EFFICIENCY OF TETRACHLOROETHYLENE
IN WATER

μ	pH				
	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	
200 $\mu\text{g/L}^*$					
0.1	1.49 $\pm$.06	1.44 $\pm$.0	1.40 $\pm$.04	1.48 $\pm$.03	
0.01	1.44 $\pm$.08	1.38 $\pm$.02	1.39 $\pm$.0	1.43 $\pm$.02	
0.001	1.19 $\pm$.03	1.31 $\pm$.10	1.07 $\pm$.09	1.19 $\pm$.04	
*Reported as 10^7 Integrator Counts					
40 $\mu\text{g/L}^*$					
0.1	2.57 $\pm$.08	2.21 $\pm$.10	1.89 $\pm$.24	2.46 $\pm$.09	
0.01	2.27 $\pm$.02	2.60 $\pm$.08	2.54 $\pm$.10	2.48 $\pm$.04	
0.001	2.53 $\pm$.12	2.18 $\pm$.03	2.15 $\pm$.06	2.68 $\pm$.01	
*Reported as 10^6 Integrator Counts					
8 $\mu\text{g/L}^*$					
0.1	3.99 $\pm$.35	4.49 $\pm$.14	3.70 $\pm$.06	4.26 $\pm$.19	
0.01	4.91 $\pm$.27	4.86 $\pm$.18	4.75 $\pm$.02	4.89 $\pm$.32	
0.001	4.76 $\pm$.17	5.09 $\pm$.18	4.93 $\pm$.05	4.63 $\pm$.23	
*Reported as 10^5 Integrator Counts					

TABLE 15. EFFECT OF pH AND IONIC STRENGTH (μ) UPON
PENTANE LLE EFFICIENCY OF BROMOFORM IN
WATER

μ	pH			
	4	6	8	10
200 $\mu\text{g/L}^*$				
0.1	3.78 $\pm$.16	3.64 $\pm$.0	3.55 $\pm$.10	3.77 $\pm$.09
0.01	3.68 $\pm$.19	3.53 $\pm$.06	3.56 $\pm$.02	3.67 $\pm$.06
0.001	3.03 $\pm$.08	3.08 $\pm$.28	2.67 $\pm$.26	3.03 $\pm$.07

*Reported as 10^6 Integrator Counts

40 $\mu\text{g/L}^*$				
0.1	6.01 $\pm$.21	5.14 $\pm$.23	4.36 $\pm$.57	5.75 $\pm$.22
0.01	5.37 $\pm$.08	6.12 $\pm$.23	5.93 $\pm$.27	5.86 $\pm$.12
0.001	5.96 $\pm$.24	5.05 $\pm$.08	4.96 $\pm$.14	6.22 $\pm$.04

*Reported as 10^5 Integrator Counts

8 $\mu\text{g/L}^*$				
0.1	8.24 $\pm$.73	9.41 $\pm$.01	7.69 $\pm$.07	8.25 $\pm$.28
0.01	10.60 $\pm$.54	10.51 $\pm$.41	10.24 $\pm$.0	10.44 $\pm$.57
0.001	10.33 $\pm$.34	10.90 $\pm$.28	10.60 $\pm$.03	10.06 $\pm$.50

*Reported as 10^4 Integrator Counts

values are within experimental error and no great significance should be drawn from the large differences in K_d . Near 100% extraction efficiency, a very small change in E can cause a very large change in K_d .

All of the partition coefficients shown in Table 10 save for DCE, are above the 60% value held to be a minimum for good analytical practice 22,32).

EFFECT OF SAMPLE CONSTITUENTS ON EXTRACTION EFFICIENCIES

Several types of variables are considered which could conceivably have an effect on extraction efficiencies, and therefore on the accuracy of the LLE method. Of particular interest are potential effects of sample pH and ionic strength, and of sodium sulfite and methanol which are added to quench residual chlorine and in the calibration process respectively. In all cases, the 20:1 LLE method was used.

Effect of Sample pH and Ionic Strength

Experiments were designed to test the effects of varying the sample pH from four to ten and of varying the ionic strength of the sample from 0 - 0.5, with volatiles in the 1 to 200 $\mu\text{g/L}$ range of concentration. All samples were extracted and analyzed in duplicate. Pentane extractions in 25 mL bottles were conducted on the five volatiles - chloroform, bromoform, tetrachloroethylene, bromodichloromethane, dibromochloromethane. Each was analyzed at three different concentrations (8, 40, 200 $\mu\text{g/L}$), three ionic strengths (.001, .01, .1), and at four pH's (4, 6, 8, 10). The data are shown in Tables 11 through 15.

In these first experiments, no statistically significant pH effect was found, and no statistically significant ionic strength effect was found for any of the compounds if all concentration data were compared. However, for the 200 $\mu\text{g/L}$ solutions alone, a decrease in ionic strength resulted in a loss in extraction efficiency, and for the 8 $\mu\text{g/L}$ solutions alone a decrease in ionic strength increased the extraction efficiency. These effects were evident for all five compounds. Contamination by the added salt is negated by the effect shown at 5 $\mu\text{g/L}$.

A second study was then designed to further investigate this effect. Five solute concentrations (0.4, 5, 40, 100, 200 $\mu\text{g/L}$) of the same compounds at four ionic strength levels (.001, .01, and analyzed in duplicate. The data are shown in Table 16. In these experiments, no effect of ionic strength on the extraction of any of the individual compounds was found. Moreover, pairwise t-tests on data for all compounds at all concentrations yielded

TABLE 16. EFFECT OF IONIC STRENGTH (μ) UPON PENTANE
LLE EFFICIENCY (20:1) OF FIVE VOLATILES
IN WATER

(ug/L)	μ^*			
	0.50	0.10	0.01	0.001
[CHCl₃]				
200	2.26±.14	2.28±.06	2.34±.05	2.40±0
100	1.15±.01	1.12±.02	0.95±.04	1.05±.14
40	0.506±.002	0.517±.002	0.502±.011	0.482±.014
5.0	8.10±.05	7.68±.18	8.02±.02	7.52±.37
0.4	0.53±.05	0.56±.01	0.49±.01	0.52±.03
[CHBrCl₂]				
200	8.30±.51	8.45±.21	8.68±.16	8.85±.01
100	4.76±.05	4.48±.10	3.96±.15	4.39±.54
40	2.19±.01	2.24±0	2.17±.05	2.09±.05
5.0	29.4±0.2	27.8±1.0	29.4±0.1	27.4±1.4
0.4	2.58±.10	2.67±.09	2.55±.01	2.62±.05
[CHBr₂Cl]				
200	7.65±.49	7.86±.25	8.05±.15	8.24±.01
100	4.22±.05	3.99±.08	3.50±.15	3.90±.50
40	1.85±.01	1.89±.01	1.84±.04	1.77±.05
5.0	21.9±0.3	20.6±0.8	21.8±0	20.3±1.1
0.4	1.28±.06	1.33±.05	1.26±.01	1.31±.04

*Reported as 10⁶ integrator counts for 200, 100, and 40 ug/L runs, and as 10⁴ counts for 5.0 and 0.4 ug/L runs.

(continued)

TABLE 16. (continued)

	(μg/L)	u*			
		0.50	0.10	0.01	0.001
[C ₂ Cl ₄]					
	200	12.5±0.8	12.8±0.4	13.1±0.2	13.3±0
	100	7.02±.03	6.60±.12	5.94±.20	6.55±.81
	40	3.18±.02	3.25±.01	3.17±.07	3.03±.08
	5.0	46.4±0.1	43.8±1.8	46.1±0.2	43.5±2.3
	0.4	3.87±.11	4.02±.14	3.87±.03	4.00±.02
[CHBr ₃]					
	200	3.22±.22	3.32±.11	3.40±.06	3.50±0
	100	1.69±.02	1.60±.03	1.39±.06	1.56±.20
	40	0.726±.005	0.745±0	0.722±.016	0.688±.018
	5.0	8.72±.14	8.24±.36	8.70±.02	8.16±.42
	0.4	0.60±.03	0.62±.03	0.58±.03	0.58±.01

*Reported as 10⁶ integrator counts for 200, 100, and 40 μg/L runs, and as 10⁴ counts for 5.0 and 0.4 μg/L runs.

TABLE 17. EFFECT OF IONIC STRENGTH VARIATIONS UPON
DENTON TAP WATER SPIKED WITH FIVE VOLATILES*

Ionic Strength**	(pH = 5.8)				
	CHCl_3^+	CHBrCl_2^+	CHBr_2Cl^+	C_2Cl_4^+	CHBr_2^+
0.1	582.2	2420	2192	3348	829.6
	555.5	2326	2104	3159	797.2
	<u>633.5</u>	<u>2657</u>	<u>2409</u>	<u>3680</u>	<u>915.4</u>
	Avg. 590.4	2468	2235	3396	847.4
	s ± 46	± 200	± 180	± 310	± 70
0.5	532.2	2203	1990	2936	754.4
	631.9	2637	2383	3506	902.4
	<u>548.7</u>	<u>2302</u>	<u>2068</u>	<u>3086</u>	<u>779.0</u>
	Avg. 571.0	2381	2147	3176	811.9
	s ± 59	± 260	± 230	± 340	± 87
1.0	666.6	2759	2495	3703	946.2
	724.0	2991	2699	4051	1024.0
	<u>554.0</u>	<u>2319</u>	<u>2075</u>	<u>2991</u>	<u>779.0</u>
	Avg. 648.2	2690	2423	3583	916.4
	s ± 100	± 400	± 370	± 630	± 140

† Data in integrator counts $\times 10^3$.

* Concentration of 40 $\mu\text{g/L}$ spiked into unpurged water.

** NaCl added to yield this ionic strength, neglecting natural ionic strength.

no statistically significant differences between results at an ionic strength of .001 vs. .50, at the 95% confidence level.

It is not clear why the first set of experiments showed some cases where the extraction efficiency appeared to change with changes in the ionic strength. However, since an instance each of increasing and decreasing effects were observed, it is presumed the effect was due to some type of experimental imprecision.

Two additional experiments with Denton tap water were carried out to see if ionic strength effects occurred in actual samples. In one experiment, unpurged Denton tap water at an unadjusted pH of about 5.8 was spiked with 40 µg/L of the same five compounds used in the previous studies. Triplicate runs were made with sodium chloride added to the samples to yield ionic strengths of 0.1, 0.5, and 1.0, presuming the natural ionic content of the sample could be neglected. The data are given in Table 17. No significant ionic strength effect was found on any individual compound. However, a statistically significant effect was found if all compound data were pooled and the 0.5 vs. the 1.0 ionic strength results were pairwise t-tested.

Another experiment used purged Denton tap water which was spiked with 40 µg/L of chloroform, bromodichloromethane, and dibromochloromethane and 25 µg/L of bromoform with additions of sodium chloride to yield ionic strengths of 0.01, 0.1, 0.3, 0.7, and 1.0 if natural ionic species were neglected. The pH of the sample was 8.87, and its conductivity before salt addition was 69 micromhos/cm. Results of triplicate analyses are given in Table 18. There was no ionic strength effect found with any individual compound. However, when the data for all compounds for an ionic strength of 0.01 were tested vs. that for 0.7, a statistically significant difference at the 95% confidence level was found. This conclusion is presumed to be a statistical anomaly and no significance is attached to it. It should be noted that the effects of ionic strength which were found in these two latter experiments only occurred at high levels (0.5 to 1.0) which are unlikely to occur in drinking water samples.

It should be further noted that ionic strengths of 0.1 and 1.0 correspond to total dissolved solids (as NaCl) of 5850 and 58,500 mg/L (ppm) respectively. These are far in excess of the ionic strengths found in drinking water supplies. Thus, for the compounds studied, no changes in extraction efficiency is expected, over the range of Total Dissolved Solids values usually found in water samples of interest. Moreover, if there is a concern over matrix effects, the LLE procedure may be slightly modified so that a (purged) water sample can be used for

TABLE 18. EFFECT OF IONIC STRENGTH UPON EXTRACTION OF FOUR VOLATILES IN PURGED DENTON TAP WATER*

Ionic Strength**	HCCl ₃ [†]	HCB ₂ Cl ₂ [†]	HCB ₂ Cl [†]	HCB ₃ [†]
0.01	732.6 693.4 655.0 <u>693.7</u> ± 46	3236 3111 2944 <u>3097</u> ±170	2743 2676 2524 <u>2648</u> ±200	759.6 723.4 687.0 <u>723.3</u> ± 65
Avg. s				
0.1	710.4 648.2 760.4 <u>706.3</u> ± 66	3165 2899 3389 <u>3151</u> ±290	2726 2481 2879 <u>2695</u> ±350	742.6 674.0 779.6 <u>732.0</u> ± 94
Avg. s				
0.3	761.4 709.6 717.8 <u>729.6</u> ± 31	3325 3186 3241 <u>3251</u> ± 82	2899 2729 2798 <u>2809</u> ±150	785.2 744.2 763.0 <u>764.1</u> ± 37
Avg. s				
0.7	809.2 762.4 697.4 <u>756.3</u> ± 66	3607 3396 3079 <u>3361</u> ±310	3130 2919 2695 <u>2915</u> ±390	854.8 792.0 730.0 <u>792.0</u> ±110
Avg. s				
1.0	744.6 819.6 649.6 <u>737.9</u> ±100	3325 3634 2940 <u>3300</u> ±410	2859 3189 2516 <u>2855</u> ±600	777.8 863.0 682.6 <u>774.5</u> ±160
Avg. s				
Purged Blank	51.2	55.0	17.6	0

* Concentration for first four compounds was 40 µg/L. Bromoform was 25 µg/L. pH was 8.9, and conductivity was 69 micromhos/cm.

** Sodium chloride was added to give this ionic strength in addition to the natural ionic content.

† Integrator counts x 10³.

TABLE 19. EFFECT OF SODIUM SULFITE UPON EXTRACTION
BY LLE OF FOUR VOLATILES IN DENTON TAP
WATER^a

Comments	(ug/L)			
	HCCl ₃	HCCl ₂ Br	HCClBr ₂	HCCl ₃ Br
No Quench	16.5	19.3	21.1	4.5
Denton Tap Water	17.0	19.5	21.0	4.4
	17.9	20.0	21.1	5.0
Avg.	17.1	19.6	21.07	4.6
s	±0.8	±0.4	±0.06	±0.4
0.001 M Quench	15.8	17.8	20.2	4.4
Denton Tap Water	16.1	17.5	19.6	4.3
	15.8	17.5	19.7	4.2
Avg.	15.9	17.6	19.8	4.3
s	±0.2	±0.2	±0.4	±0.1
No Quench	21.7	25.6	26.8	8.0
Spiked at 6 ppb ⁺	21.4	26.6	27.8	8.3
(HCCl ₃ , 3.5 ppb)	20.2	21.2	22.8	7.8
Avg.	21.1	24.5	25.8	8.0
s	±0.9	±3	±3	±0.3
0.001 M Quench	20.3	23.0	24.6	8.7
Spiked at 6 ppb	21.6	23.2	27.8	8.3
(HCCl ₃ , 3.5 ppb)	20.2	21.2	22.8	7.8
Avg.	20.7	22.5	25.1	8.3
s	±0.8	±1	±3	±0.5
No Quench	55.9	53.2	54.0	29.5
Spiked at 42 ppb ⁺	53.9	60.1	60.9	28.6
(HCCl ₃ , 25 ppb)	54.0	60.9	61.4	28.7
Avg.	54.6	58.1	58.8	28.9
s	±1	±5	±4	±0.5
0.001 M Quench	50.1	49.2	52.6	28.5
Spiked at 42 ppb	52.5	59.7	60.7	28.9
(HCCl ₃ , 25 ppb)	50.9	57.8	59.1	27.8
Avg.	51.2	55.6	57.4	28.4
s	±1	±6	±5	±0.7

(continued)

TABLE 19. (continued)

Comments	(μg/L)			
	HCCl ₃	HCB ₂ Cl ₂	HCB ₂ Cl	HCB ₃
No Quench	90.5	89.8	91.5	52.0
Spiked at 106 ppb ^a	93.9	89.5	89.6	51.4
(HCB ₃ , 62 ppb)	94.8	91.7	93.5	53.3
Avg.	93.1	90.3	91.5	52.2
s	±3	±1	±2	±1
0.001 M Quench	95.8	92.8	95.3	54.4
Spiked at 106 ppb	92.4	90.2	92.2	52.2
(HCB ₃ , 62 ppb)	97.4	99.6	101.4	56.7
Avg.	95.2	94.2	96.3	54.4
s	±3	±6	±6	±3

^aUnpurged.

+Spikes were actually: HCCl₃ (6.03, 42.2, 106 ppb); HCB₂Cl₂ (6.11, 42.8, 107 ppb); HCB₂Cl (6.00, 42.0, 105 ppb); HCB₃ (3.51, 24.6, 61.5 ppb).

calibration purposes. This should negate any inaccuracies caused by the use of reagent water in the calibration.

In summary, no pH effect upon the extraction efficiencies of the five compounds studied was found in any experiment with standards in pure water or in Denton tap water. An ionic strength effect upon the extraction efficiencies of standards in pure water was found in one experiment but was not confirmed in later experiments. Studies of this effect in Denton tap water shows its occurrence only at high ionic strengths (0.5 to 1.0) and only if all compound information is pooled. There was no evidence to support an ionic strength effect upon the extraction efficiency of an individual compound under these experimental conditions.

Effect of Quenching Agent

A series of experiments were carried out to determine the effect of sodium sulfite on the extraction efficiency of the THMs in unpurged Denton tap water. Samples spiked with from 0 to 106 $\mu\text{g/L}$ of the compounds, except for bromoform which was 0 to 62 $\mu\text{g/L}$, were analyzed in triplicate both with and without the addition of 126 mg/L of sodium sulfite. The tap water contained 17 $\mu\text{g/L}$ HCCl_3 , 20 $\mu\text{g/L}$ HCBBrCl_2 , 21 $\mu\text{g/L}$ HCBBr_2Cl , and 4.6 $\mu\text{g/L}$ HCBBr_3 before spiking or adding quench. The data are shown in Table 19 as actual concentrations of THMs (internal standard method). No statistically significant difference was found between quenched and unquenched samples by pairwise t-testing at the 99% confidence level. However, the unspiked tap water did show 5 to 10% differences for dibromochloromethane and bromodichloromethane respectively upon quench addition. These differences were only statistically significant at the 95% confidence level. The Denton tap water apparently contained very little residual chlorine, or the reactions leading to the production of the THMs were at completion at the time of analysis. Since this is not always the case with every water sample, it is advisable to add a quench before analysis.

Effect of Methanol

Experiments were designed to determine the effect of methanol, which is used to prepare the standards, upon the extraction efficiencies of the LLE method. Additions of 0, 0.1%, and 1.0% (V/V) of Allied Electronic Grade absolute methanol were made to reagent water spiked with 0, 6, 42, and 106 $\mu\text{g/L}$ of chloroform, bromodichloromethane, and dibromochloromethane. The corresponding bromoform spikes were 0, 3.5, 25, and 62 $\mu\text{g/L}$. These samples were extracted in triplicate and analyzed by the usual procedure. The resulting data are shown in Table 20. The

blank water runs with and without the addition of 1% methanol showed only small contaminations of 0.2 $\mu\text{g/L}$ bromodichloromethane and 0.06 $\mu\text{g/L}$ chloroform from the methanol even at the 1% level.

The results showed no statistically significant difference between the data sets at the 99% confidence level except for chloroform spiked at the 42 $\mu\text{g/L}$ level and containing 0.1 and 1% methanol. The difference found was an increase of 19% upon going from 0.1 to 1.0% methanol. Since this effect was not consistently found at all spiking levels, we consider it to be a statistical fluctuation and not real. Pairwise t-testing gave differences at the 95% confidence level for chloroform at the 6 $\mu\text{g/L}$ spike level (0 vs. 0.1% methanol), at the 106 $\mu\text{g/L}$ spike level (0.1% vs. 1.0%), and at the 42 $\mu\text{g/L}$ spike level (0 vs. 1%). A similar effect was found at the same confidence level for bromodichloromethane spiked at the 42 $\mu\text{g/L}$ level in the 0.1 vs. 1.0% data. Since the final methanol concentration of the standards in water is in the range of 0.03 to 0.1%, the apparent effects found for the 0.1 to 1.0% methanol solutions are not important to the method in actual practice.

In summary, methanol and sodium sulfite do not appear to have a measurable effect on the LLE method, at least at the concentrations used in the recommended procedure. The results with methanol are in agreement with those reported by Richard and Junk (16).

CHOICE OF SOLVENT FOR THE LLE METHOD

The ideal solvent for the LLE method for volatile organics would satisfy the following criteria:

- (I) ready availability at relatively low cost in a form pure enough to use directly;
- (II) GC retention and detection characteristics so that the solvent itself would not interfere with the detection of analytes at low ($\mu\text{g/L}$) levels;
- (III) nontoxic and relatively safe to use in typical laboratories.

In the course of this project, several solvents were investigated with these criteria in mind. Richard and Junk (16), Mierue (15) and EPA (1) have published similar criteria.

It is generally agreed that volatile organohalides are best analyzed with an aliphatic hydrocarbon solvent (1). For the analysis of THMs, several choices are available including n-

TABLE 20. EFFECT OF METHANOL UPON THE EXTRACTION OF
FOUR VOLATILES BY LLE^a

Comments	(ug/L)			
	HCCl ₃	HCCl ₂ Br	CHCl ₂ Br	CHBr ₃
Blank Water	0.40	0.08		
0% Methanol	0.38	0.08		
	0.41	0.07		
Avg.	0.40	0.077		
s	±0.02	±0.006		
Blank Water	0.44	0.28		
1% Methanol	0.48	0.33		
	0.47	0.30		
Avg.	0.46	0.30		
s	±0.02	±0.03		
0% Methanol	6.93	7.60	6.89	3.62
Spiked at 6 ppb+	6.30	7.03	6.38	3.31
(HCCl ₃ , 3.5 ppb)	5.79	6.44	5.84	3.03
Avg.	6.34	7.02	6.37	3.32
s	±0.7	±0.7	±0.6	±0.4
0.1% Methanol	6.34	8.96	9.28	4.95
Spiked at 6 ppb	5.19	7.35	7.36	4.01
(HCCl ₃ , 3.5 ppb)	5.77	8.15	8.32	4.48
Avg.	5.77	8.15	8.32	4.48
s	±1	±1	±2	±0.9
1.0% Methanol	6.71	7.46	6.81	3.56
Spiked at 6 ppb	6.14	6.99	6.34	3.28
(HCCl ₃ , 3.5 ppb)	5.46	6.38	5.80	3.03
Avg.	6.10	6.94	6.32	3.29
s	±0.8	±0.7	±0.6	±0.3
0% Methanol	42.2	42.8	42.0	24.6
Spiked at 42 ppb+	41.7	42.6	41.8	24.5
(HCCl ₃ , 25 ppb)	41.3	42.5	41.9	24.7
Avg.	41.7	42.6	41.9	24.6
s	±0.5	±0.2	±0.1	±0.1

(continued)

TABLE 20 (continued)

Comments	(µg/L)			
	HCCl ₃	HCB ₂ Cl ₂	HCB ₂ Cl	HCB ₃
0.1% Methanol	38.6	39.8	40.2	23.8
Spiked at 42 ppb	41.4	43.4	43.7	24.0
(HCB ₃ , 25 ppb)	42.2	44.4	44.6	26.3
Avg.	40.7	42.5	42.8	24.7
s	±2	±3	±3	±2
1.0% Methanol	46.3	43.1	42.0	24.4
Spiked at 42 ppb	48.2	44.9	42.0	25.6
(HCB ₃ , 25 ppb)	50.7	46.7	45.9	27.0
Avg.	48.4	44.9	43.3	25.7
s	±3	±2	±2	±2
0% Methanol	86.3	82.8	83.1	52.9
Spiked at 106 ppb†	92.7	88.2	89.0	57.3
(HCB ₃ , 62 ppb)	92.2	88.6	89.2	57.2
Avg.	90.4	86.5	87.1	55.8
s	±4	±4	±4	±3
0.1% Methanol	93.5	93.3	94.3	60.5
Spiked at 106 ppb	87.3	90.7	93.5	61.1
(HCB ₃ , 62 ppb)	88.5	90.5	91.4	58.3
Avg.	89.8	91.5	93.1	60.0
s	±4	±2	±2	±2
1.0% Methanol	99.7	92.1	92.2	58.8
Spiked at 106 ppb	98.5	90.6	90.9	58.3
(HCB ₃ , 62 ppb)	100.3	92.8	93.4	60.1
Avg.	99.5	91.8	92.2	59.1
s	±1	±1	±1	±1

a

"Organic-free water" was used as the matrix.

†Actual spikes were: HCCl₃ (6.03, 42.2, 106 ppb); HCB₂Cl₂ (6.11, 42.8, 107 ppb); HCB₂Cl (6.00, 42.0, 105 ppb); HCB₃ (3.51, 24.6, 61.5 ppb).

pentane, n-hexane, methylcyclohexane, and isooctane. Other than readily available purity, which is discussed in the next section, there is little to speak against any of these four solvents. There may be some cases where n-pentane is not preferred when laboratory temperatures are high ($>25^{\circ}\text{C}$), but refrigerators may be used to cool samples and syringes to avoid any problem.

When organohalides other than the THMs are analyzed, n-pentane or a high boiling solvent becomes preferable. In this case, the eluting solvent peak will usually have some effect on the analysis as shown in Figure 5. Here a low concentration standard in n-pentane is compared to pure solvent runs. The latter show baseline aberrations due to elution of solvent at the positions marked by the arrow. Although these effects will not be severe at higher concentrations of analytes, they may be entirely avoided with n-pentane.

When one wishes to use GC/MS* as a confirmatory tool for LLE analyses, or if FID is the detection method, n-pentane or a high boiling solvent is even more imperative. In both cases, it is essential for the solvent to be removed (chromatographically speaking) from the analytes. Applications of the LLE procedure for the analysis of aromatics is discussed in a later section, and the requirement for a low boiling solvent is evident in these studies.

In summary, n-pentane appears to be the solvent of choice for the LLE method for organohalides and aromatics. For THMs other aliphatic solvents may be used, and in cases where ambient laboratory temperatures are warm, these other solvents may be preferable to n-pentane. Availability of pure grades of solvents is discussed in the following section.

EFFECT OF SOLVENT PURITY ON THE LLE METHOD

It is clear that the application of the LLE is critically dependent on the availability of a solvent which is essentially free of interfering substances. To obtain some information of the purity of commercially available hydrocarbon solvents, a survey was conducted using gas chromatography with EC detection

*GC/MS in the negative ion/chemical ionization mode (30) may not require n-pentane for the solvent, depending on the concentration of analytes. However, spectra of compounds which elute near the solvent will probably be affected.

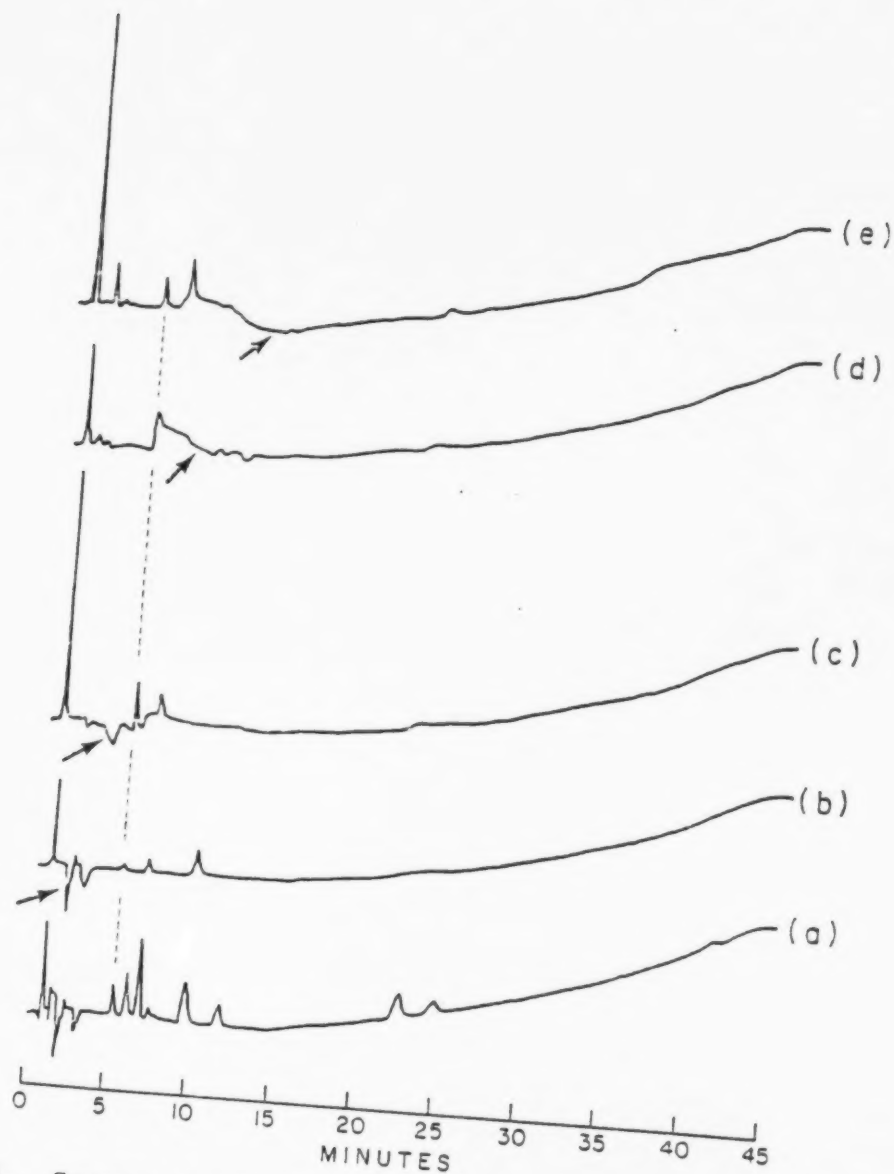


Figure 5. Survey chromatogram (mixed phase column, 6% OV-11/4% SP-2100) of 9 compound organohalide standard (4 $\mu\text{g/L}$ each) in n-pentane (a) compared to pure solvent injections: (b) n-pentane; (c) n-hexane; (d) isooctane; (e) methylcyclohexane.

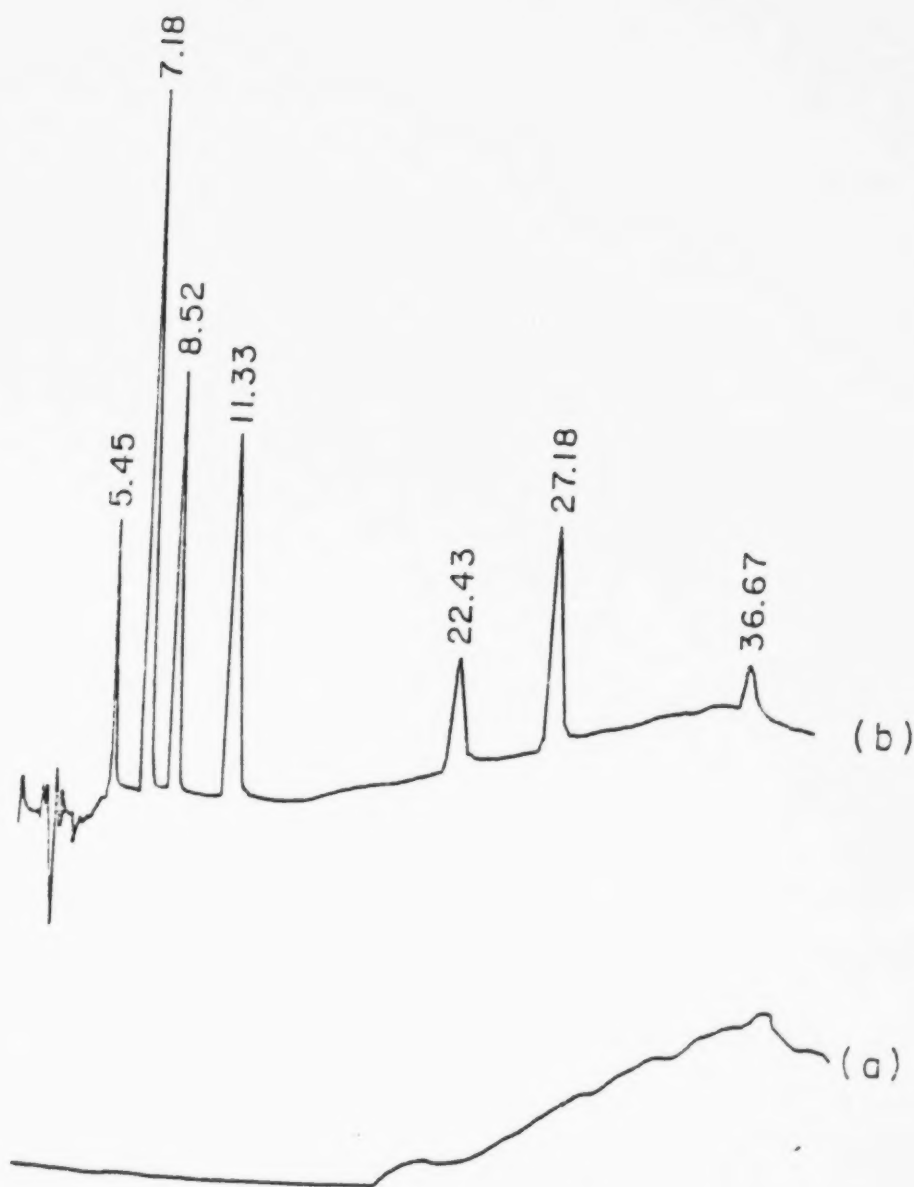


Figure 6. Column blank (a) and standard mixture of VOAs (b) on 10% SP-2100 column. Retention times of standards: 5.45 (CHCl_3); 7.18 (1,1,1-trichloroethane); 8.52 (CCl_4); 11.33 (CHBrCl_2) and CHCl=CCl_2 ; 22.43 (CHBr_2Cl); 27.18 (C_2Cl_4); 36.67 (CHBr_3). EC attenuation $2^{6.2}$; 2 μL injection.

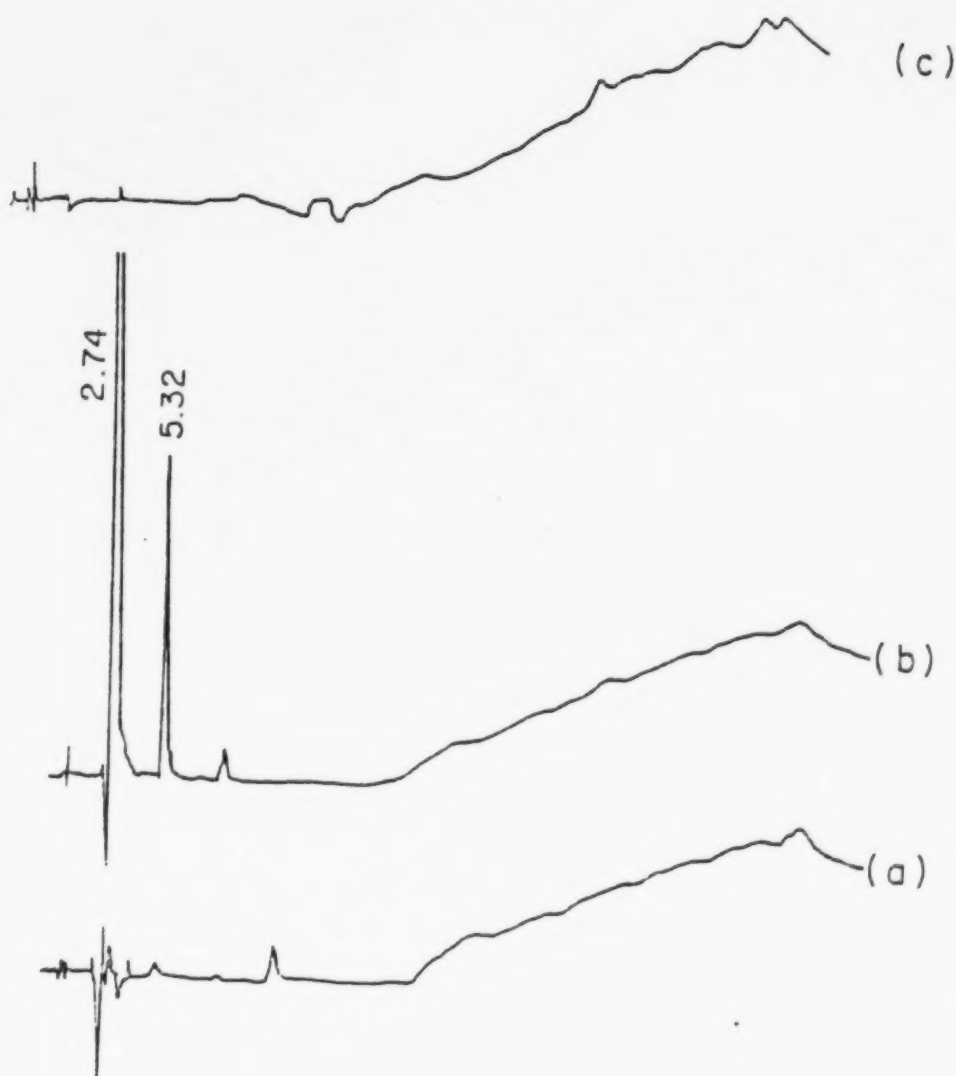


Figure 7. Survey chromatograms (10% SP-2100 column) of commercial solvents. (a) Fisher pesticide grade n-pentane; (b) Burdick & Jackson pesticide grade n-pentane; (c) Fisher isooctane, redistilled from sodium. EC attenuation 2^6 ; 2 μ L injection.

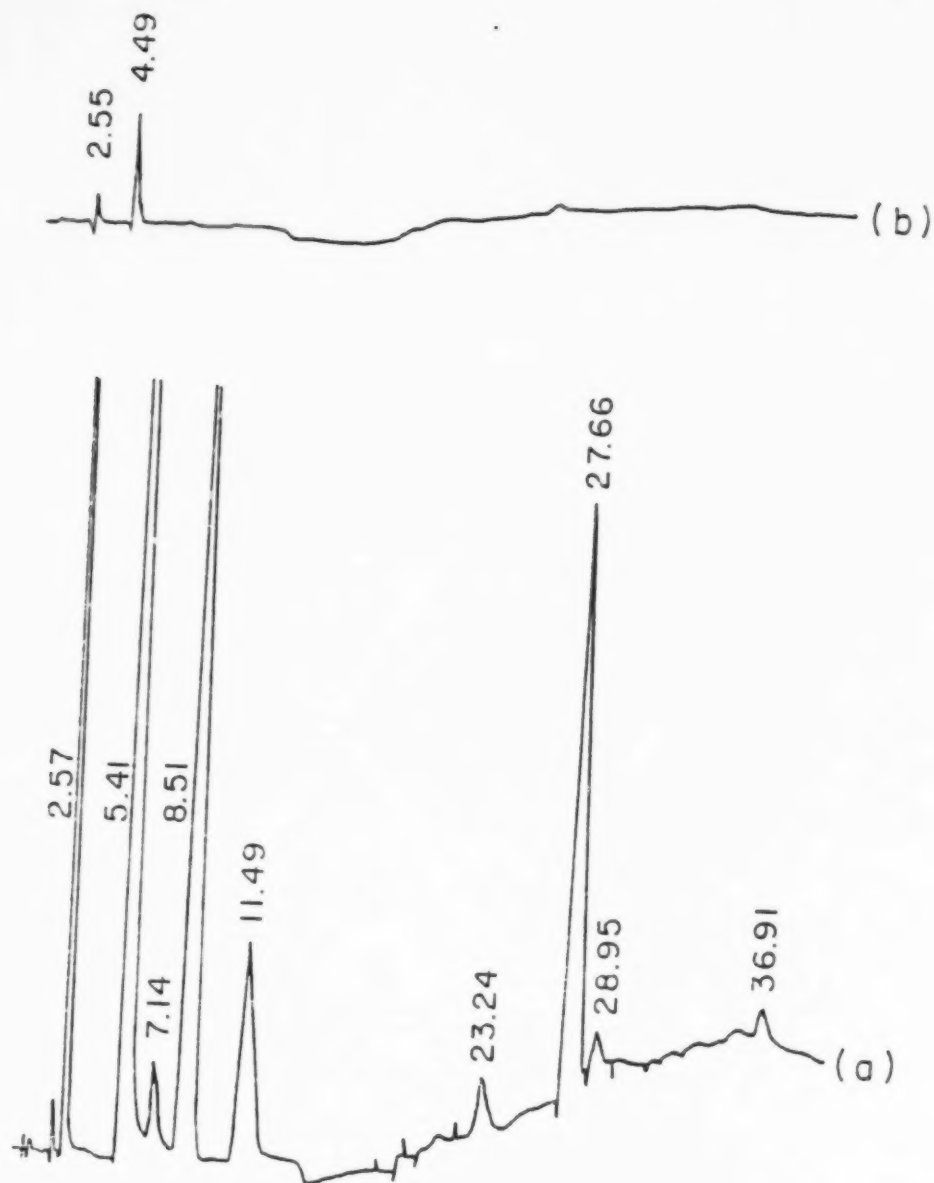


Figure 8. Survey chromatogram (10% SP-2100 column).
 (a) Aldrich 99% methylcyclohexane. EC attenuation 2^6 ;
 (b) Mallinckrodt or grade methylcyclohexane. EC
 attenuation 2^6 . 2 μ L injections.

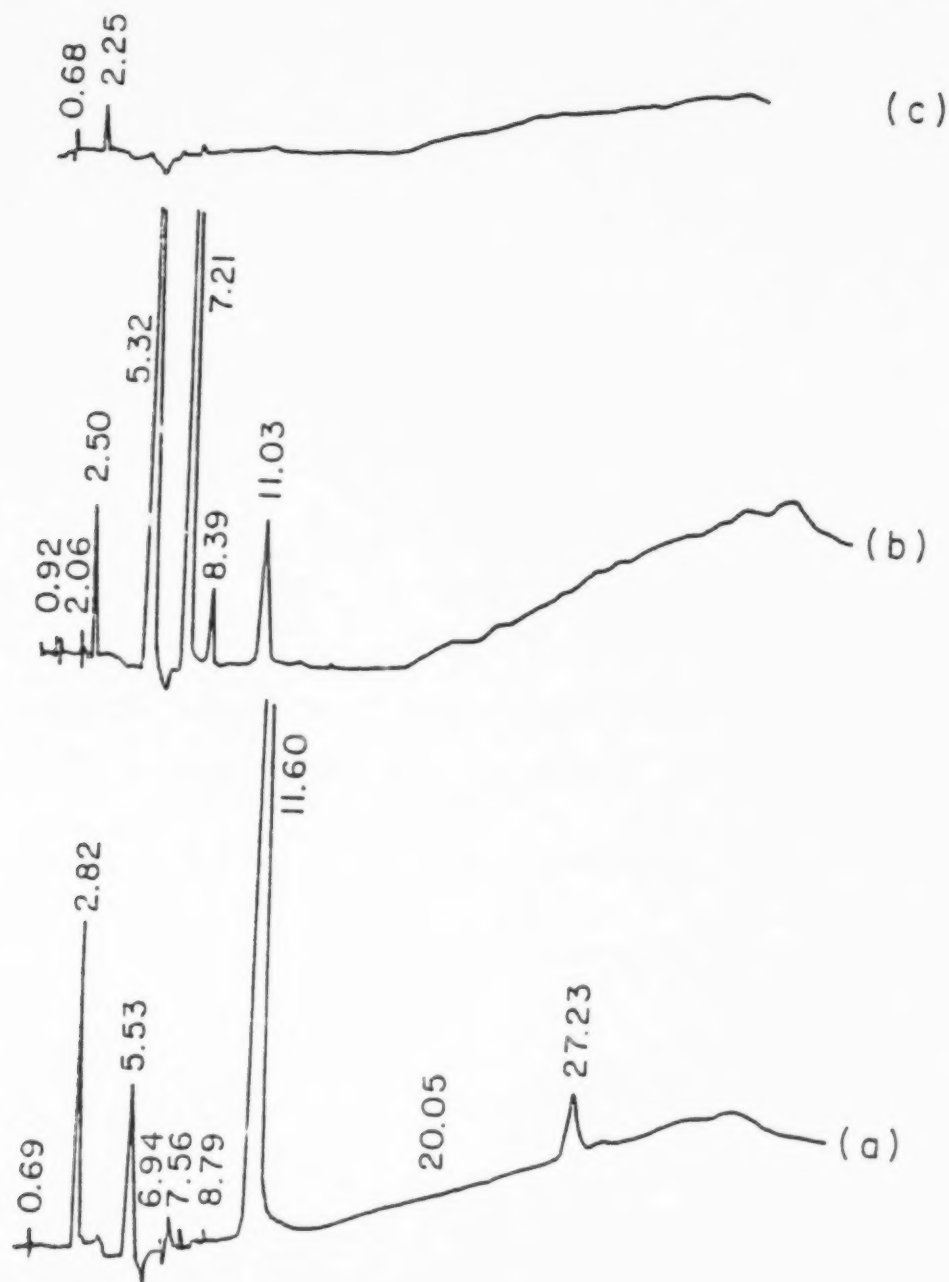


Figure 9. Survey chromatogram (10% SP-2100 column) of commercial solvents (a) Burdick and Jackson UV grade n-hexane; (b) Mallinckrodt chromar grade n-hexane; (c) Mallinckrodt chromar grade n-hexane after alumina treatment. EC attenuation 2^6 ; 2 μ L injection.

as the examining tool. A column containing 10% SP-2100 liquid phase was used with the following temperature program: 35° for 14 minutes, 1°C/min. to end of run, about 40 minutes (Figures 6-9). Column background and a 20 µg/L standard of organohalides are shown in Figure 6.

Four solvents were chosen for initial examination: n-pentane, n-hexane, isooctane, and methylcyclohexane. A complete list of the suppliers is given in Table 21. Note that Mallinckrodt methylcyclohexane was run with an attenuation of 2⁸, while all other work was done at an attenuation of 2⁶. The isooctane had been previously purified by sodium distillation in the laboratory.

Batches of Fisher pentane were shown to be quite free from substances which would interfere with the analysis of volatile organohalides (Figure 7a). Except for a small amount of some low boiler (integral of 35,000 for the peak at 4.49; about 35 µg/L if chloroform), Mallinckrodt methylcyclohexane was found to be very clean for LLE work (Figure 8b). Solvents from all other sources contained large quantities of interfering compounds and would require further purification for use as an LLE solvent (Figures 7-9).

TABLE 21. PURITY OF SOLVENTS OBTAINED FROM VARIOUS SUPPLIERS

Figure	Solvent	Supplier	Grade
(4)	<u>n</u> -pentane	Fisher	Pesticide
(4)	<u>n</u> -pentane	Burdick & Jackson	Pesticide
(4)	<u>isooctane</u> (NA distilled)	Fisher	(Unknown)
(5)	<u>n</u> -hexane	Burdick & Jackson	UV
(5)	<u>n</u> -hexane	Mallinckrodt	ChromAR
(6)	methylcyclohexane	Aldrich	99%
(6)	methylcyclohexane	Mallinckrodt	OR

A simple method of solvent purification was reported by Richard and Junk (16), which requires neither heating nor a

dangerous reducing agent. A glass column was filled with basic alumina (Super IW 200, ICN), with no pretreatment or rinse; the alumina column was 15 in. x 3/4 in. i.d. and contained some 125 g of alumina. Mallinckrodt hexane, containing at least four contaminating compounds (Figure 9b) was selected as the test solvent for cleanup. The hexane was poured through the alumina, and the flow rate was found to be about 3 mL/min., depending upon the quantity of solvent at the head of the column. Two experiments with this solvent, each with a fresh alumina column, showed that some four bed-volumes (300 mL) of this particular solvent batch could be purified very well. Presumably, a cleaner initial solvent would require less purification, so that more solvent could be handled per gram of alumina. Figure 9c shows an SP-2100 chromatogram of this purified hexane; this particular 5 mL sample was collected after 300 mL had previously been run through the column. An attempt to purify Aldrich methylcyclohexane with alumina also proved successful. While fairly expensive (\$6 for alumina to clean up 300 mL of an already costly solvent), this provided ample solvent for a number of runs, and in a very convenient manner.

GAS CHROMATOGRAPHIC CONDITIONS FOR THE LLE METHOD

This project included the evaluation of packed column and capillary (wall coated open tubular, WCOT) columns for the separation of trihalomethanes and other halogenated and/or aromatic organics. The solvent for most of these studies was n-pentane, the preferred solvent for the LLE method.

Optimization of GC conditions was attempted, considering both column selection and analysis parameters. In the case of packed columns, several liquid phases were tried for the purpose of eventually specifying at least two different columns in order to confirm THMs or other VOCs without the aid of GC/MS.

Packed Column Separation of THMs

This is not a difficult separation and may be accomplished with several types of columns. Henderson et al. (14) specified a 2 m x 2 mm i.d. glass column with 10% squalane on Chromosorb W/AW, 80/100. Baseline separation of the four THMs was accomplished within a total analysis time of less than eight minutes. In the original paper, chromatographic conditions were as follows: column temperature, 67°C; injection port temperature, 100°C; argon/methane (90/10) carrier gas flow rate: 20 mL/min. with 60 mL/min. as makeup gas to detector. Figure 10 shows a typical chromatogram obtained under slightly different conditions, illustrating that the separation may be easily accomplished on this column.

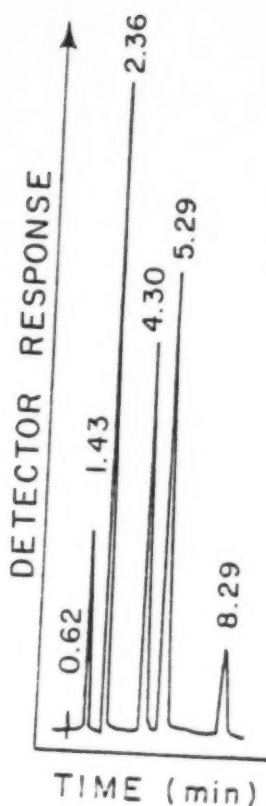


Figure 10. Typical gas chromatogram of 40 $\mu\text{g/L}$ standard of four THMs with 10% squalane on chromosorb A/AW. Column temperature, 80°; injection port temperature, 100°; Ni^{63} C temperature 300°; attenuation, 2^{12} ; flow rate of helium, 21 mL/min.; retention times: 1.43 (CHCl_3); 2.36 (CHBrCl_2); 4.30 (CHBr_2Cl); 5.29 ($1,2\text{-C}_2\text{H}_4\text{Br}_2$, internal standard); 8.29 (CHBr_3).

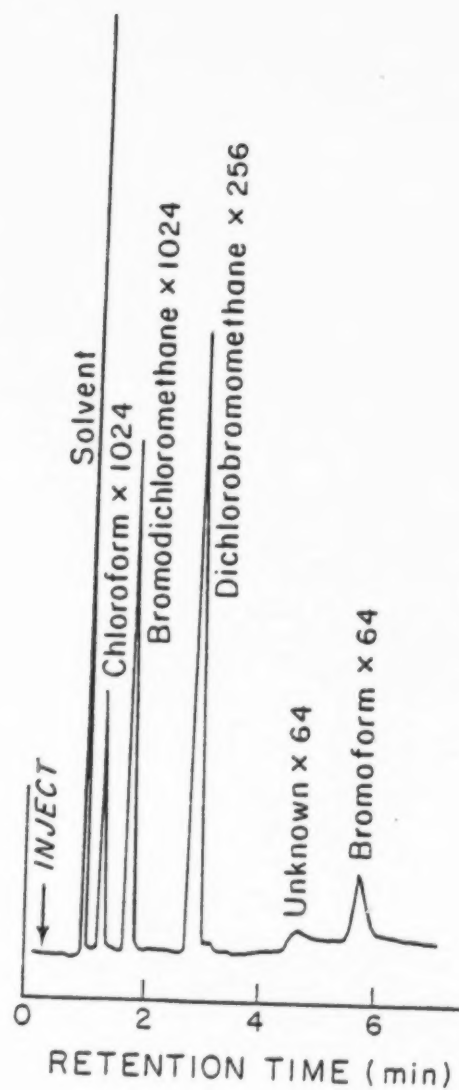


Figure 11. Gas chromatogram of finished water extract (1). 2 m x 2 mm i.d. glass column with 3% SP-1000 on Supelcoport (100/120 mesh) at 50°C; 60 mL/min. flow rate (5% methane in argon); ECD.

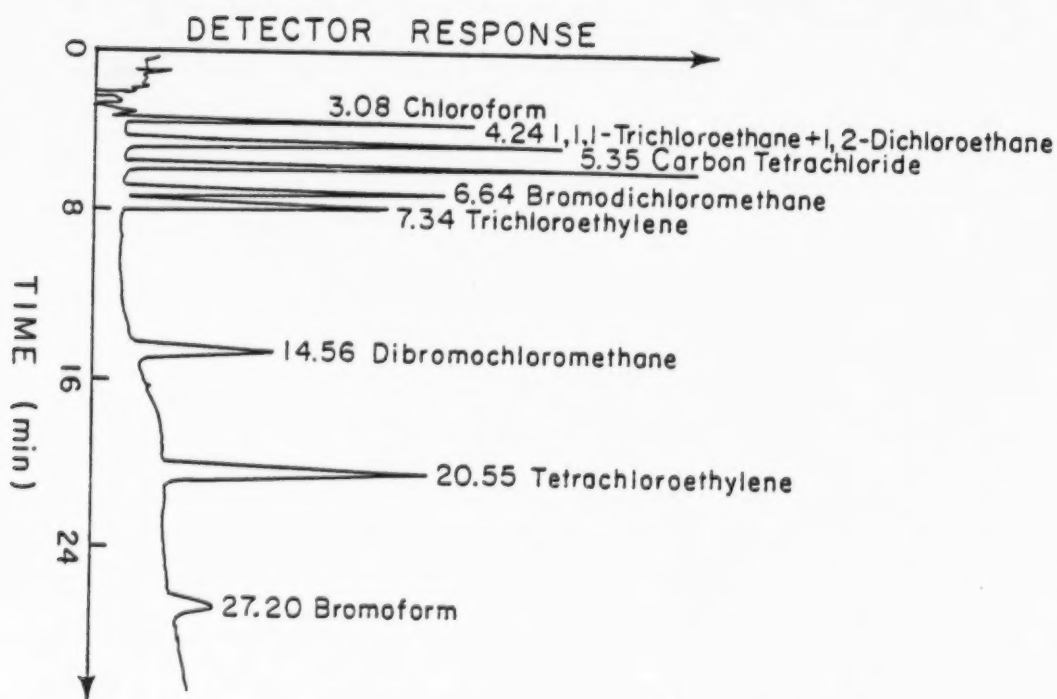


Figure 12. Temperature programmed GC analysis of nine-compound standard with 12.5% squalane on 80/100 chromosorb W/AW. Column temperature: 45°C, 8 min.; 1°C/min. to end of run.

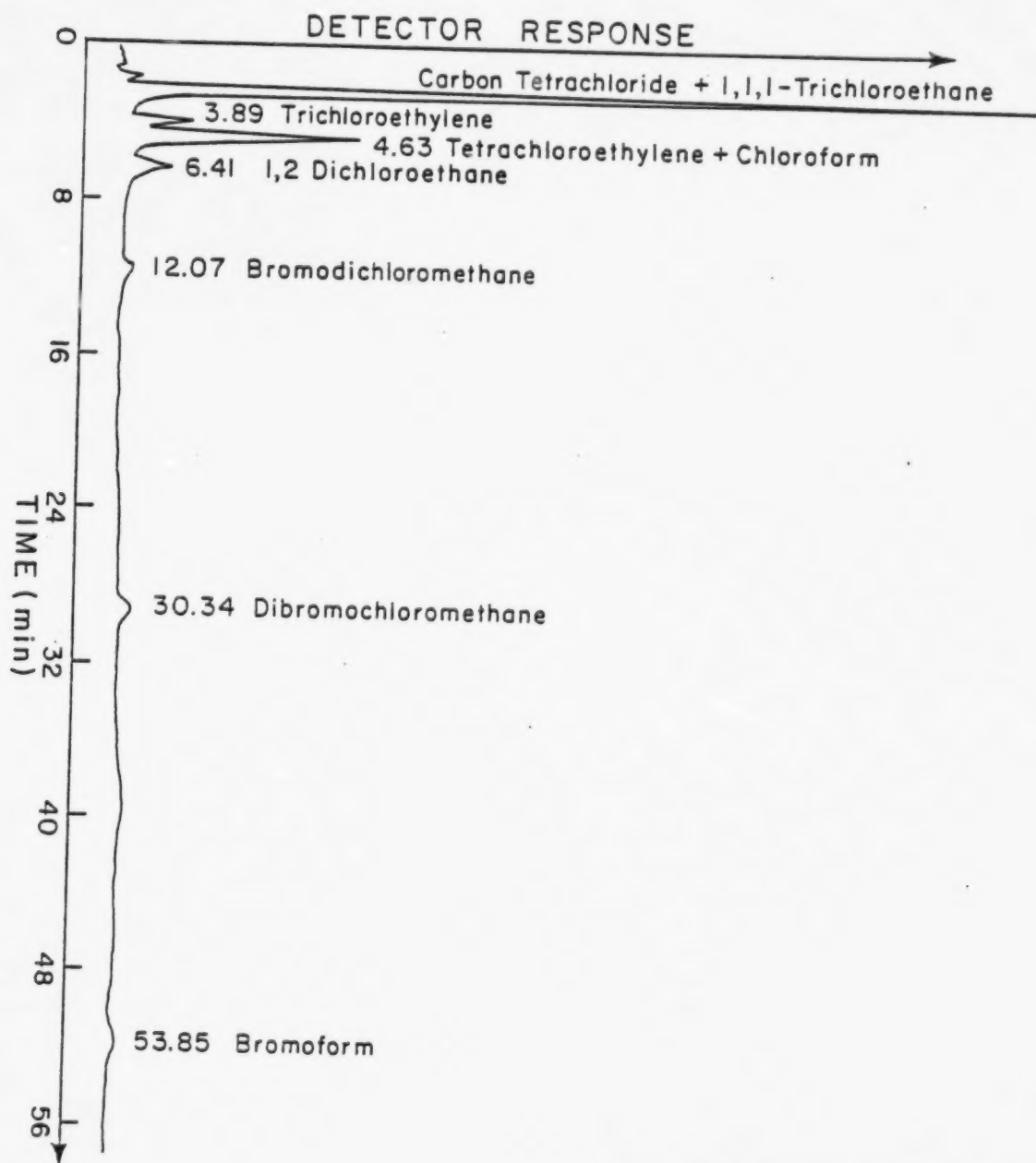


Figure 13. Temperature programmed GC analysis of nine-compound standard with 3% SP-1000 on 100/120 Supelcoport. Column temperature: 35°C, 15 min.; 1°C/min. to end of run.

Squalane is also specified as one column of choice in the EPA-approved method (1). In addition, a second column with a 3% SP-1000 liquid phase is also specified. Figure 11 is a chromatogram of a finished water extract taken from the EPA method.

In summary, several GC columns are capable of resolving the four common THMs. The columns specified in the EPA procedure are a good combination of columns with different polarities as needed for dual column confirmation studies.

Packed Column Separation of Volatile Organohalides

In addition to the THMs, other volatile organohalides are now known to occur in drinking water sources in the United States (2). In the early stages of the present project, nine of these compounds, including the THMs were used to evaluate packed columns for GC separation. The compounds used were the THMs; carbon tetrachloride; 1,2-dichloroethane; 1,1,1-trichloroethane; trichloroethylene; and tetrachloroethylene.

The initial liquid phase investigated was squalane, since previous work had shown good THM resolution with a 10% squalane column. Also studied were SP-1000, SP-2100, OV-11, Apiezon M, and a mixed phase column of Carbowax 20M and a 6-ring polyphenyl ether. All coatings were done in the lab, except for the SP-1000 which was purchased precoated. All columns were 9' x 2 mm i.d., unless otherwise noted. Evaluations were made by 2 μ L injections of a pentane solution containing the nine compounds listed above; dichloroethane was at a concentration of 80 μ g/L, while the remainder were each at a concentration of 20 μ g/L.

Three squalane loadings were investigated: 10%, 12.5%, and 18%, all on 80/100 Chromosorb W/AW. The 10% loading could not resolve bromodichloromethane and trichloroethylene, even at 28°C; the higher loadings did give baseline resolution of eight peaks at temperatures near ambient. One peak contained both of the chlorinated ethanes, precluding their quantitation with this column when both are present in a system. All other compounds of interest can be readily quantitated with the 12.5% squalane column. As shown in Figure 12, total time for the analysis is under 30 minutes, with the conditions as follows: flow, 20 mL/min.; injector, 100°C; oven, 45°C for 8 minutes, then programmed 1°C/min. until completion of the run (57°C at 30 min.). Increasing flow or initial temperature to decrease analysis time generally resulted in poorer resolution, as well as a decrease in the integrated area of some peaks. Dropping the injector port temperature to 50°C had no affect on the separation.

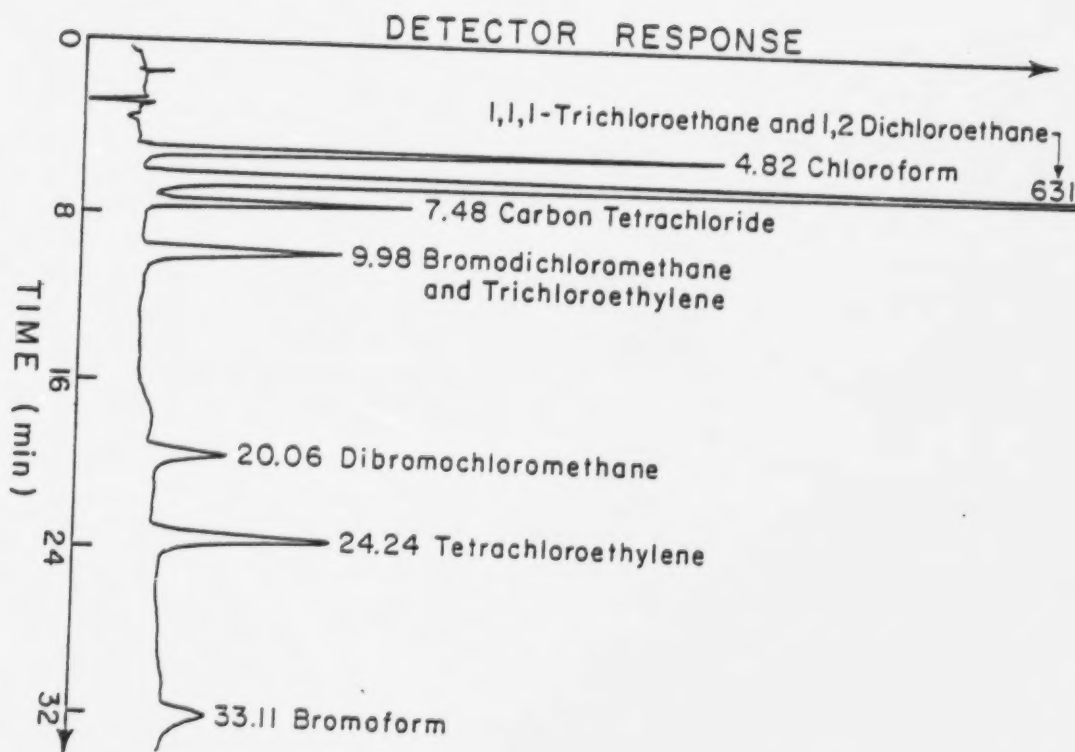


Figure 14. Temperature programmed GC analysis of nine-compound standard with 10% SP-2100 on 100/120 Supelcoport. Column temperature: 35°, 14 min.; 1°C/min. to end of run.

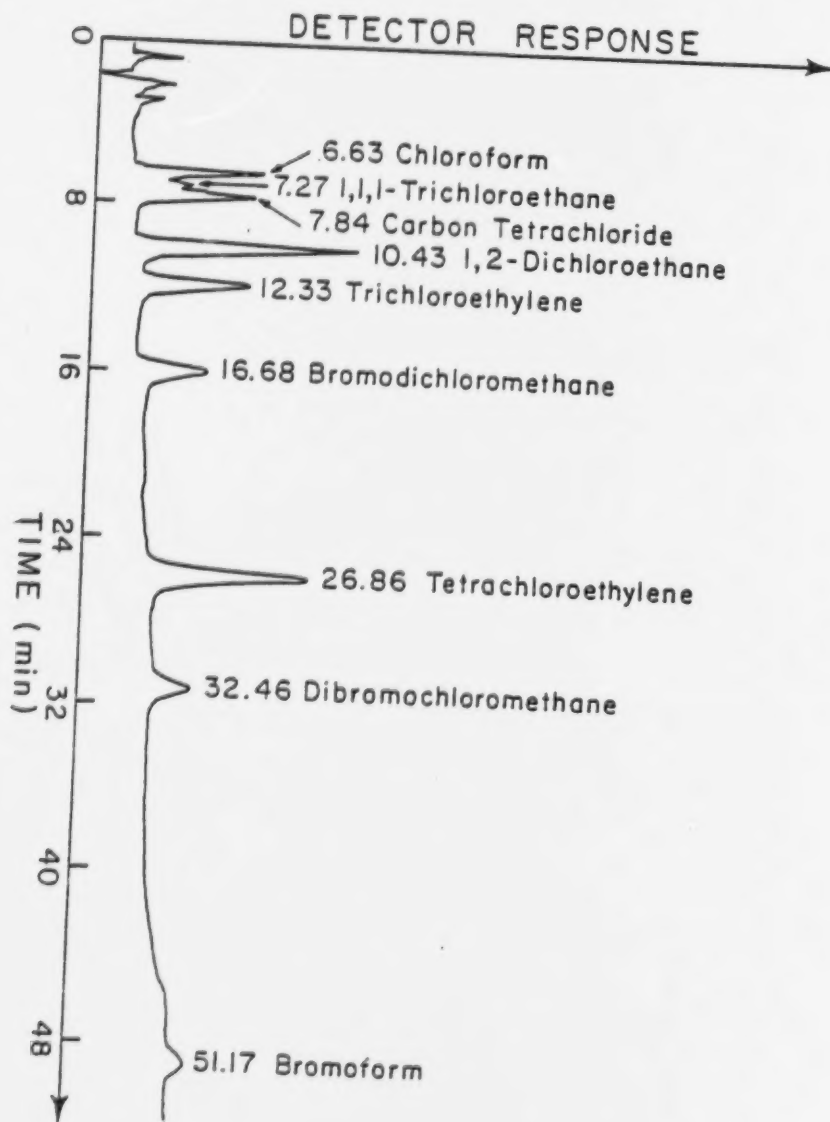


Figure 15. Temperature programmed GC analysis of nine-compound standard with 10% OV-11 on 100/120 Supelcoport. Column temperature: 35°, 15 min.; 1°C/min. to end of run.

A 3% SP-1000 column on 100/120 Supelcoport effected some separation with the following conditions: flow, 20 mL/min.; injector, 100°C; oven, 35° for 15 minutes, then programmed 1°C/min. and held at 60°C until the 55 minute analysis was completed (Figure 13). Peaks 1 and 3 represent two compounds each, and the second and third are unresolved. The analysis was quite lengthy, with poor resolution.

Two other columns also gave unsatisfactory performance: the 10% Apiezon M column and the mixed phase column of Carbowax 20M and 6-ring polyphenyl ether, each at a 10% concentration on 80/100 Chromosorb W/AW. Neither gave any real resolution of the nine compound mixture.

A methylsilicone phase (10% SP-2100 on 100/120 Supelcoport) was almost as effective as squalane for separation of this mixture. Analysis of a 40 µg/L mixture is shown in Figure 14. Di- and trichloroethanes were again not separated, and bromodichloromethane and trichloroethylene were also combined in one peak. Analytical conditions were as follows: injector at 100°C; flow, 20 mL/min.; oven, 35°C for 14 minutes, then programmed at 1°C/min. until completion of the analysis (61°C at 40 minutes).

An OV-11 column was made (10% on 100/120 Supelcoport) and used, but the resolution of chloroform, carbon tetrachloride, and 1,1,1-trichloroethane was poor (Figure 15). For the first time, however, the two chloroethanes had been resolved with good peak shape. In fact, with this column, they eluted better than three minutes apart.

The results described in the previous two paragraphs suggested that a liquid phase with polarity between that of OV-11 (a silicone polymer with 35% phenyl, 65% methyl substituents) and SP-2100 (a pure methylsilicone polymer), might be successful for the desired purpose. To predict the approximate composition of this ideal liquid phase, a mixed phase composition/retention time plot was prepared for the nine compound mixture. Figure 16 is such a plot, with the intersections on each vertical axis being the retention times of the compounds on the two pure liquid phase. Tie lines connect these two points for each compound.

Figure 16 suggested three possible ratios of SP-2100: OV-11 which might be suitable for the separation: 80:20; 50:50; and 40:60. To hold the analysis time to a minimum, and because of the good resolution by the methyl silicone phase (SP-2100) of the three low boilers mentioned in a preceding paragraph, it was decided to first try a higher percentage of SP-2100. An 8% SP-2100 + 2% OV-11 mixture was coated on 100/120 Supelcoport, and a

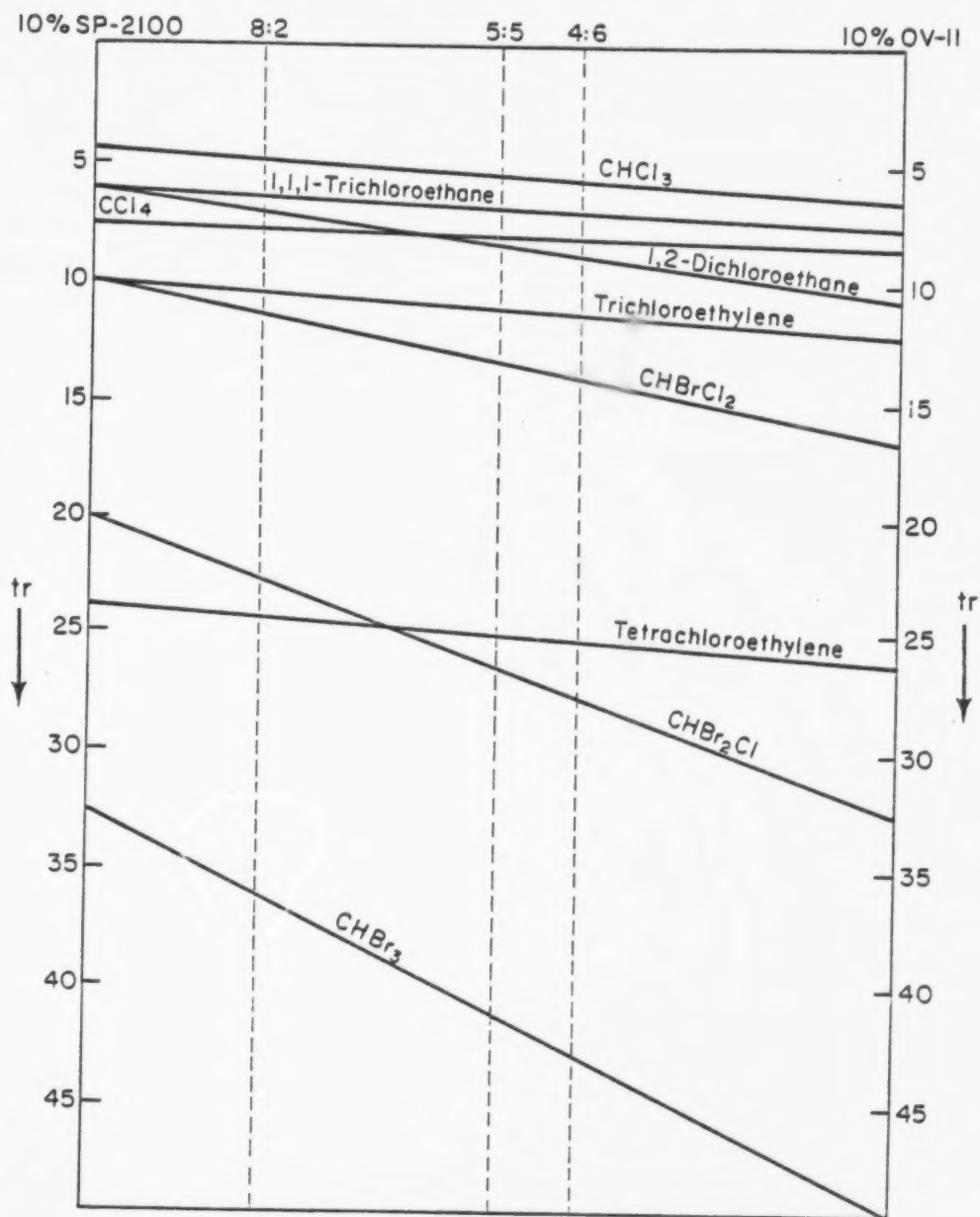


Figure 16. Mixed phase retention time diagram for nine organohalides. tr: retention time; conditions for determining tr given in text.

nine-foot column was subsequently packed and evaluated. A 35-minute analysis time was achieved with good resolution of all compounds, except for some overlap on either side of 1,2-dichloroethane (Figure 17). In the absence of dichloroethane, this would be an excellent column, with a short analysis time even from a 35°C starting temperature.

Two additional mixes of SP-2100 and OV-11 were tried: the first was 5% in each of the liquid phases, and the second was 6% in OV-11 and 4% SP-2100. These columns moved the elution time for dichloroethane past that for carbon tetrachloride, and the second of these gave good baseline resolution for all nine compounds. Figure 18 shows the chromatogram of the nine-compound mixture on the 4:6 column with dichloroethane at 400 µg/L and the others at 100 µg/L each. The program was 45°C for 12 minutes, then 1°C/min. to 70°C, with a 25 mL/min. flow.

The mixed phase column, 6% OV-11 and 4% SP-2100, appears to be a good primary column, with good resolution and an analysis time of 40 minutes. A comparison of retention times for the nine compounds on this mixed phase column and on the 12.5% squalane column (Table 22) shows significant differences for all compounds, so that identification could be confirmed using these two columns.

TABLE 22. RETENTION TIMES FOR NINE COMPOUNDS ON SQUALANE AND A MIXED PHASE PACKING

Compound	Retention Times: Actual and Relative			
	12.5% on squalane		6% OV-11/4% SP-2100	
	Time (min)	Relative to CHCl ₃	Time (min)	Relative to CHCl ₃
Chloroform	3.08	1.00	4.41	1.00
1,1,1-Trichloroethane	4.24	1.38	5.72	1.30
1,2-Dichloroethane	4.24	1.38	7.00	1.59
Carbon tetrachloride	5.35	1.74	6.37	1.44
Bromodichloromethane	6.64	2.16	10.96	2.49
Trichloroethylene	7.34	2.38	9.11	2.05
Dibromochloromethane	14.56	4.73	23.14	5.25
Tetrachloroethylene	20.55	6.67	21.08	4.78
Bromoform	27.20	8.93	39.38	8.93

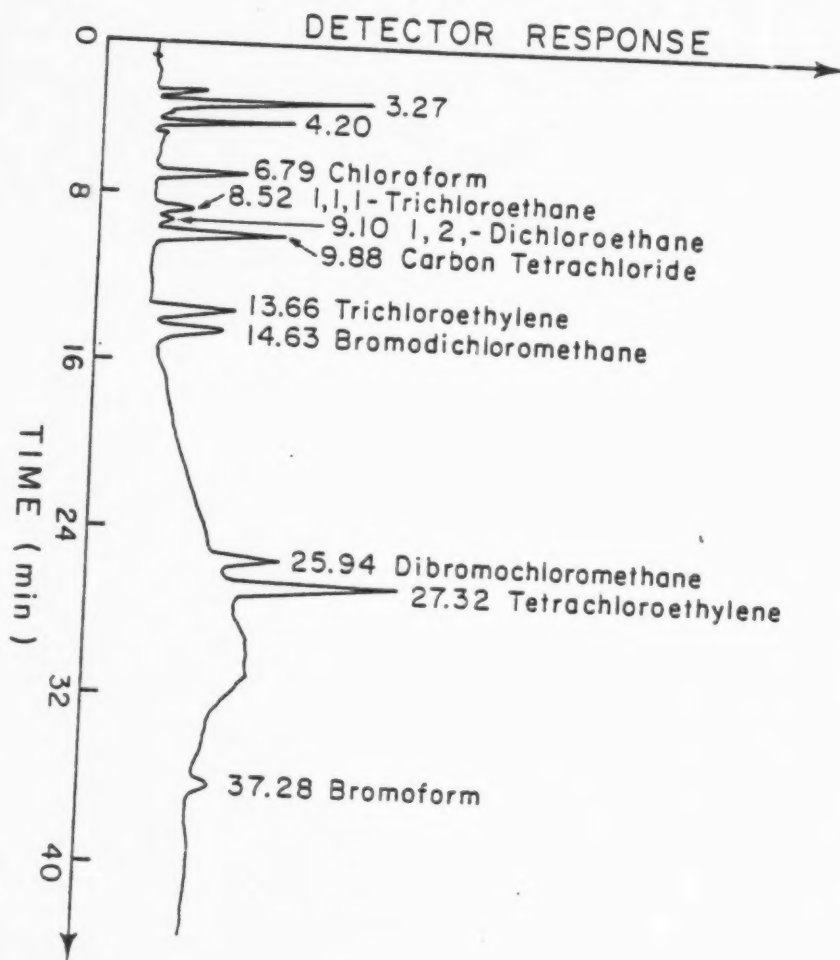


Figure 17. Temperature programmed GC analysis of nine-compound standard on mixed phase column containing 8% SP-2100, 2% OV-11 on 100/120 Supelcoport. Column temperature: 35°, 14 min.; 2°C/min. to end of run.

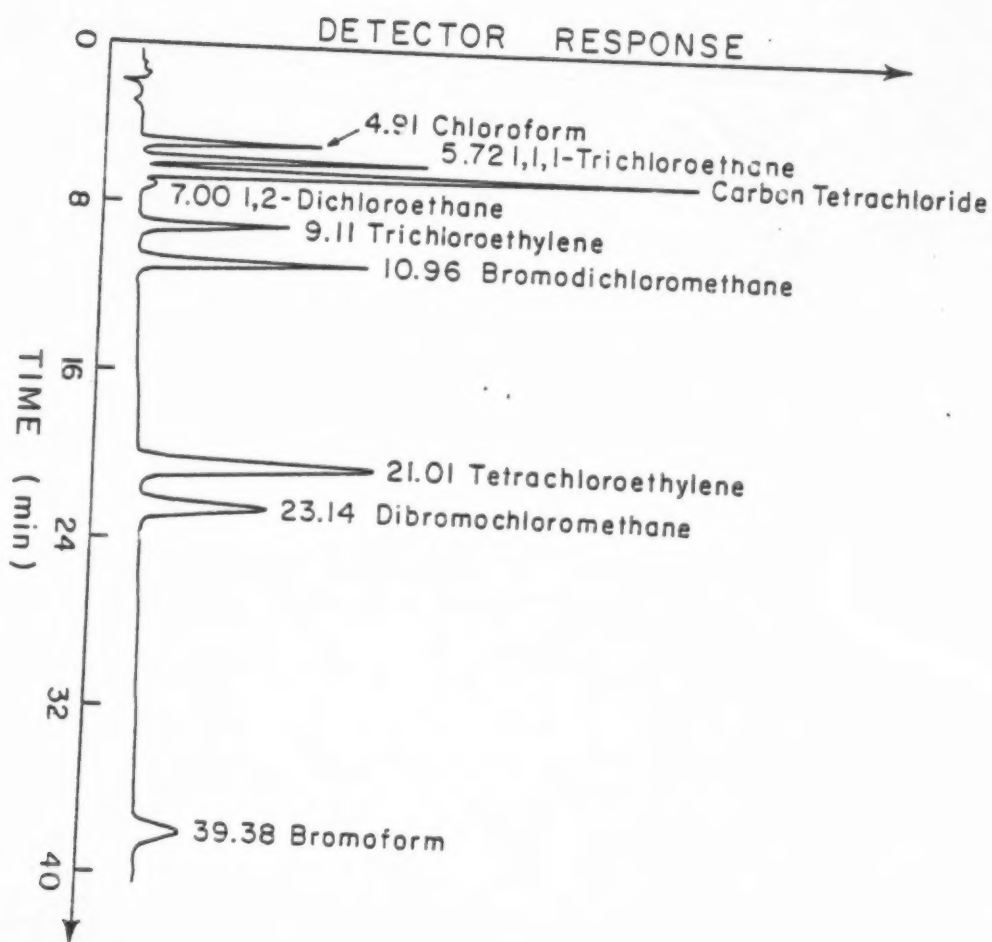


Figure 18. Temperature programmed GC analysis of nine-compound standard on mixed phase column containing 6% OV-11 and 4% SP-2100. Column temperature: 45°, 12 min.; 1°C/min. to 70°C.

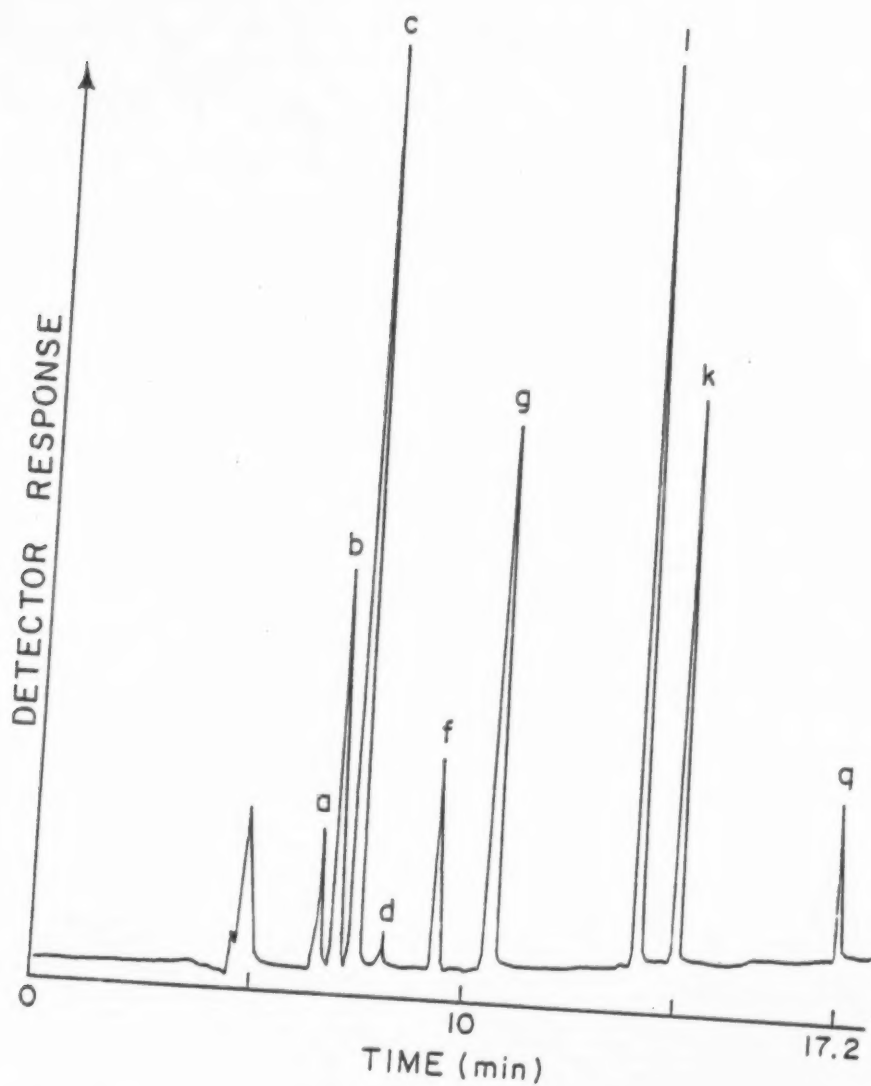


Figure 19. Chromatogram of nine-compound organohalide mixture on glass WCOT column with 3:2 OV-11/SP-2100. Code in Table 23; conditions in text.

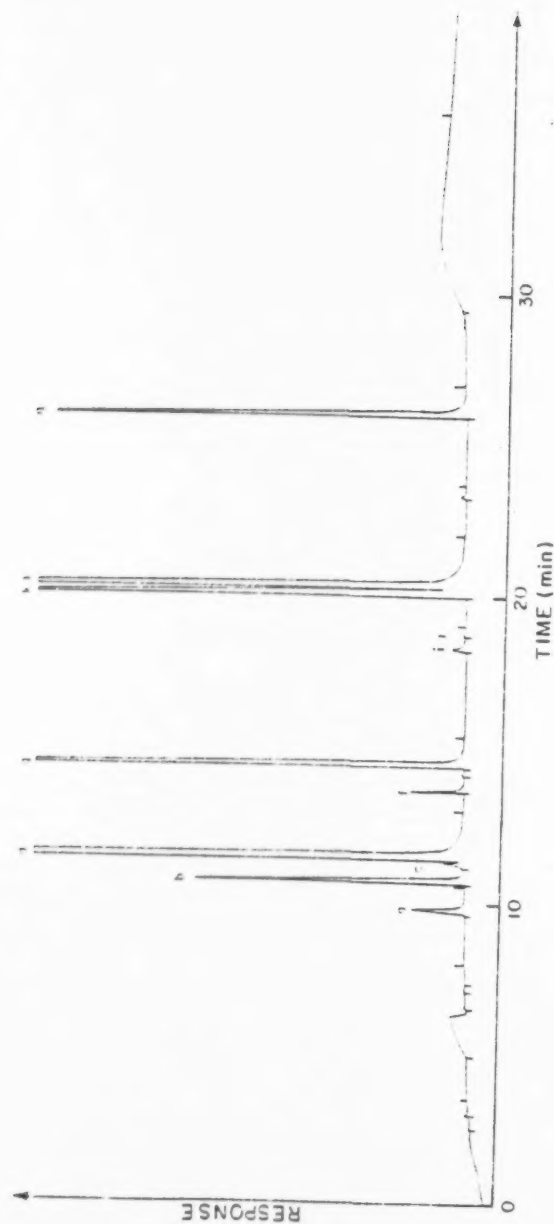


Figure 20. ^{63}Ni electron capture gas chromatogram of volatile organic compound standard. Code listed in Table 24; WCOT glass column with SE-54; 60 m x 0.25 mm i.d.; purge delay for splitless injection: 0.5 min.; septum purge, 4 mL/min.; inlet purge, 70 mL/min.; temperature program: 0°C, 1 min.; 3°C/min. to 110°C; helium carrier gas velocity, 31 cm/sec. at 0°C; make-up gas to detector, 50 mL/min. Ar/CH₄.

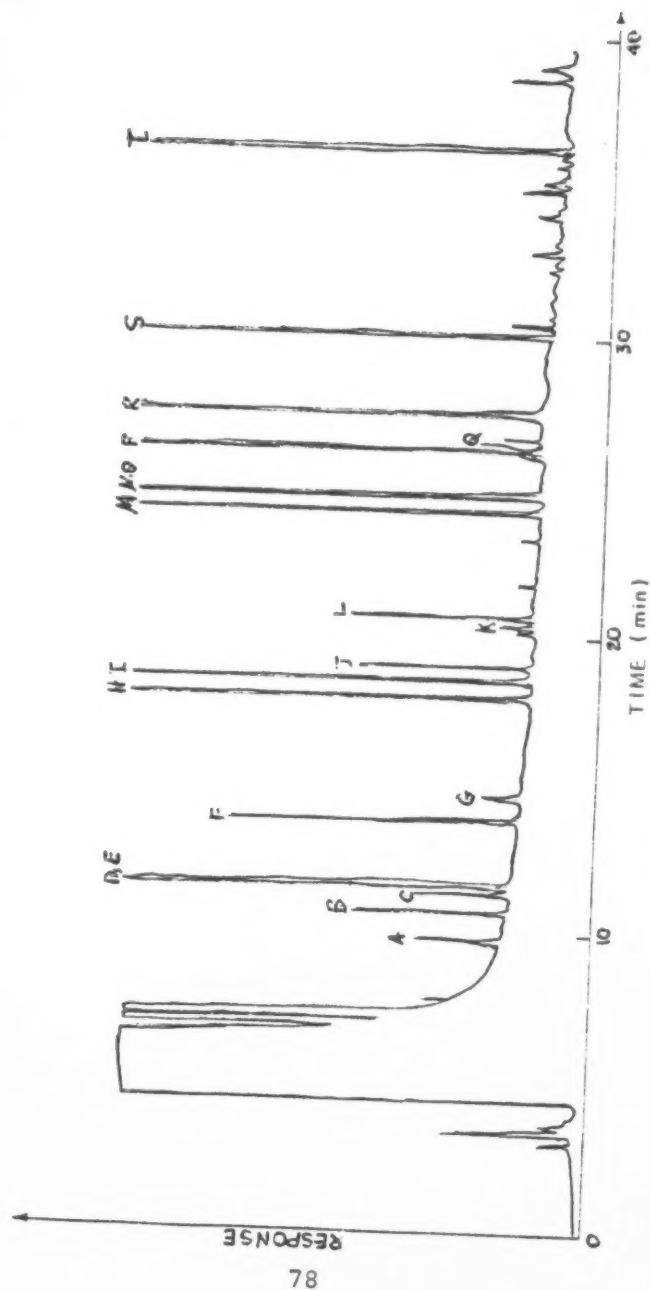


Figure 21. Flame ionization gas chromatogram of volatile organic compound standard, SE-54 capillary column. See Table 24 for compound code and Figure 20 for conditions (helium rather than Ar/CH₄ to detector).

Glass Capillary Column Separation of Volatile Organics

In the initial phases of this work, wall coated open tubular (WCOT) glass capillary columns were investigated for the separation of the nine-compound organohalide mixture. Several liquid phases (wall coatings) were tried, including SP-2100, OV-11 and mixed phases.

Figure 19 shows a chromatogram of a nine-compound standard with 300 mg of each compound injected, except for 1,2-dichloroethane and bromoform, which were 6000 ng and 150 ng respectively. Conditions were as follows: 1 μ L, splitless injection; helium gas velocity of 20 cm/sec.; injection temperature 200°C; electron capture detector temperature of 300°C; temperature program: 20°C for 0.5 min., 1°C/min. for 8 minutes, and then 8°C/min. to end of run. Excellent separation was achieved for 1,1,1-trichloroethane, carbon tetrachloride, and 1,2-dichloroethane which were not well separated on the packed column. The total run required only 18 minutes compared to 40 minutes for a packed column run (Figure 18).

The power of WCOT columns is shown in Figures 20 and 21, which illustrate the separations achieved with a 60 m x 0.25 mm i.d. glass column with SE-54* liquid phase. Both chromatograms are of a *n*-pentane extract of a spiked drinking water sample containing the organic compounds shown in Table 23.

Concentrations of the original water sample were those shown above, and the extraction ratio V_w/V_s was 240. At an estimated extraction efficiency of 50% for each compound, this would correspond to a concentration factor of approximately 120 from water to pentane. Thus, a compound at 25 μ g/L in water would be 3000 μ g/L in the pentane, or 3 ng/ μ L. Since a 1 μ L injection was made, Figures 20 and 21 then show the separation and detector response for approximately 3 ng of each compound.

More germane to the purposes of this section is the separation achieved in the WCOT column. Figure 20, the ^{63}Ni EC chromatogram shows poorer resolution of the 1,2-dichloroethane and carbon tetrachloride than the mixed phase column shown in Figure 19. Moreover, the chlorodibromomethane and tetrachloroethylene are not well resolved. Nonetheless, with the

* Se-54 is a methyl silicone polymer with 5% phenyl and 1% vinyl substituents (General Electric trademark).

TABLE 23. CODE FOR COMPOUNDS ANALYZED BY CAPILLARY GC

Code	Compound	µg/L
a	Chloroform	
b	1,1,1-Trichloroethane	20
c	1,2-Dichloroethane	21
d	Carbon tetrachloride	23
e	Benzene	23
f	Trichloroethylene	24
g	Bromodichloromethane	26
h	Toluene	27
i	1,Chloro-2-bromopropane (1)	23
j	1,1,2-Trichloroethane (2)	
k	Chlorodibromomethane	
l	Tetrachloroethylene	25
m	Ethylbenzene	20
n	<u>p</u> -Xylene	22
o	<u>m</u> -Xylene	24
p	<u>o</u> -Xylene	28
q	Bromoform	23
r	1,4-Dichlorobutane (1)	27
s	<u>n</u> -Propylbenzene	
t	<u>n</u> -Butylbenzene	30
		28

(1) Internal standard.

(2) Values not known.

exception of 1,2-dichloroethane, the column gives sufficient separation for the quantification of the other eight compounds.

Figure 21 shows a feature of WCOT columns which has not yet been illustrated; namely the capability to separate n-pentane solvent from aromatic hydrocarbons of interest. In this case a flame ionization detector was used, and the resulting chromatogram is a good indicator of the resolving power of the 60 m SE-54 column. Two retention time redundancies occur; between the pairs carbon tetrachloride/benzene and bromoform/o-xylene. Fortunately, the relative response factors of the members of each pair on FID and ECD are convenient. Under most conditions, one can assume with confidence that FID and ECD will allow quantification of the hydrocarbon or the halide, respectively, without significant interference from the other member of the

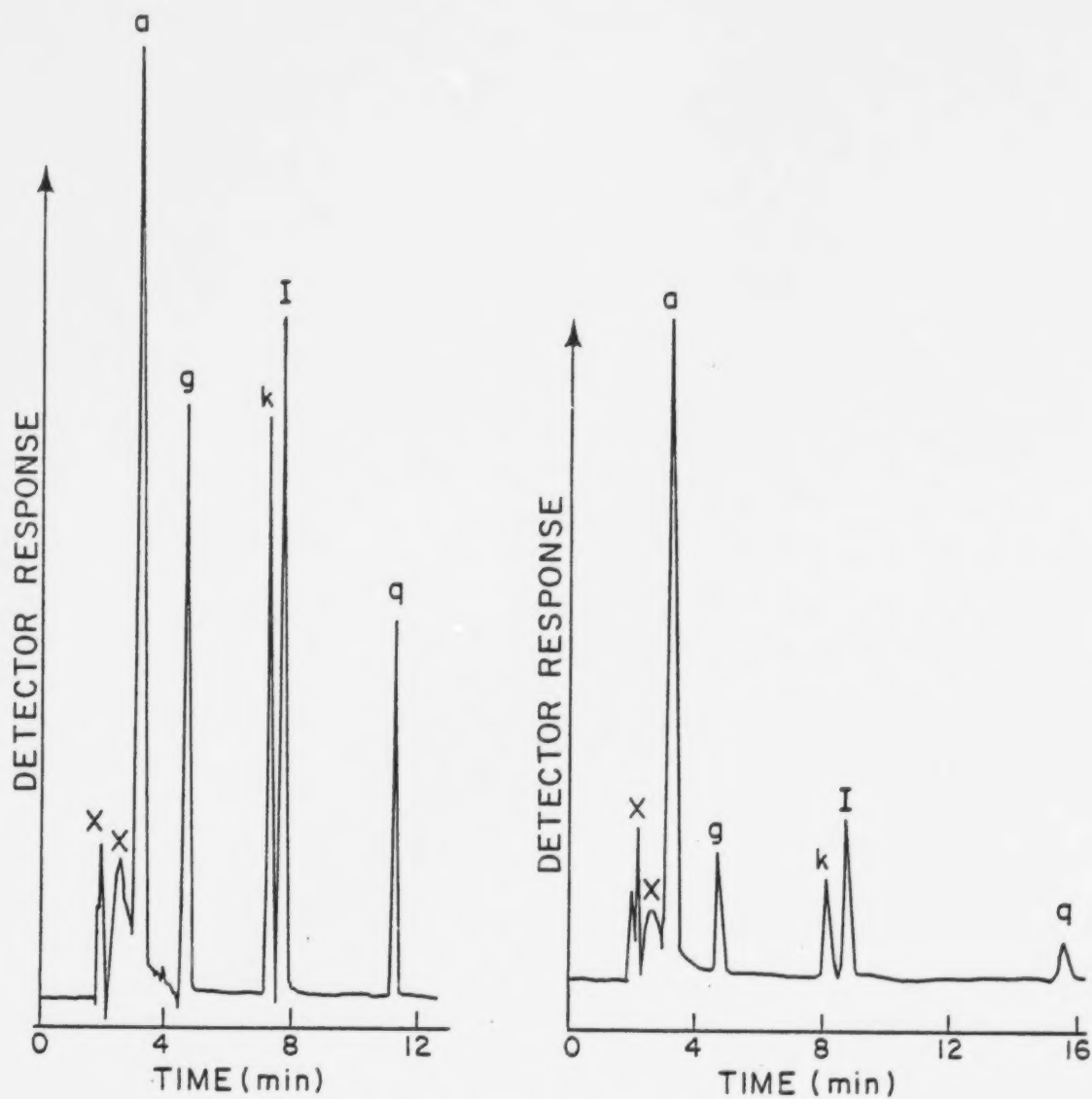


Figure 22. Fused silica capillary column chromatography (SE-54) of the four THMs in *n*-pentane and internal standard (see Table 23 for code and text for conditions). Right: 40°C, isothermal; left: 40°C, 3 minutes; 3°C/min. to end of run (X = solvent impurity).

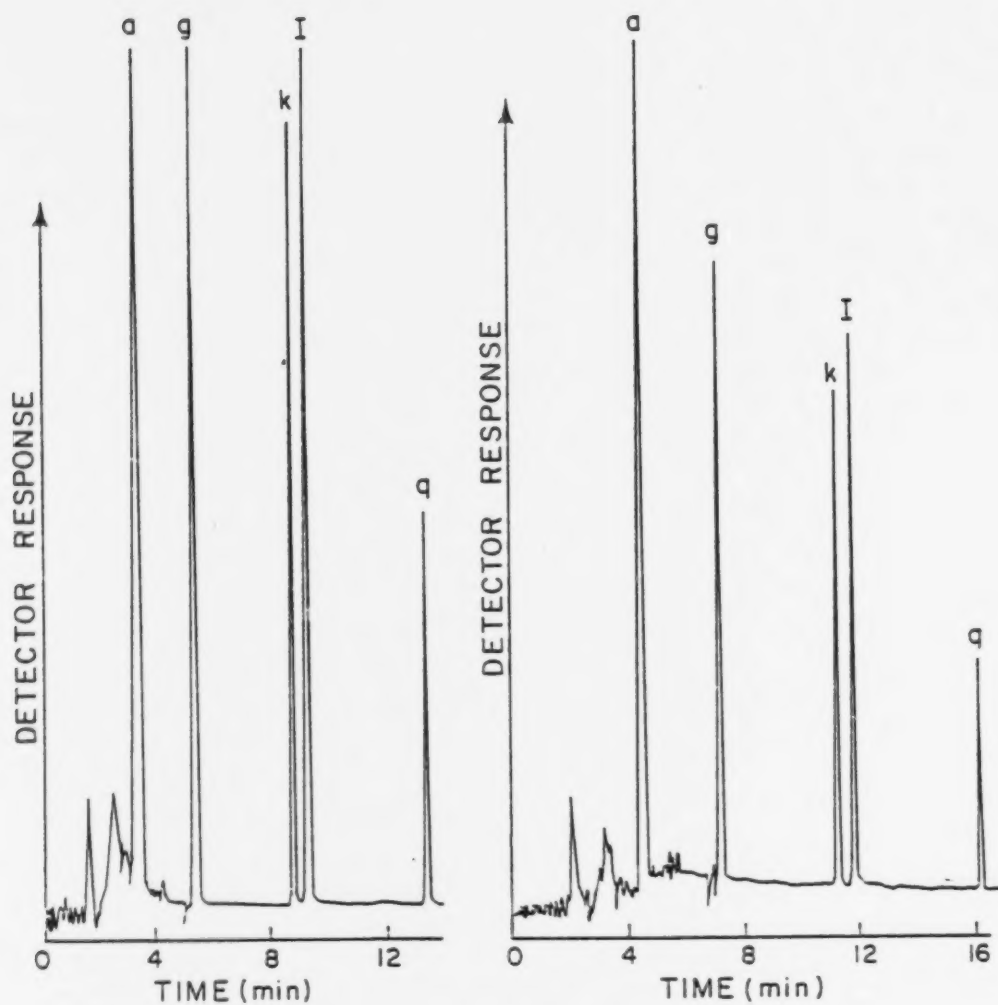


Figure 23. Fused silica capillary column chromatograph (SE-54) of the four THMs in *n*-pentane and internal standards (see Table 23 for code and text for conditions. Right: initial temperature, 20°C; left, 30°C.

pair.

More details on the detection limits of organohalides and aromatics are given in a following part of this section. Suffice it to say at this point that mixtures of these substances may be analyzed by WCOT chromatography with a combination of EC and FI detectors. As in all GC studies of environmental samples, confirmation is required unless the sample type is well defined. For this purpose, GC/MS remains the method of choice: a discussion follows.

Fused Silica Capillary Columns

Concurrent with work begun on this study, fused silica open tubular (FSOT) capillary columns became available from Hewlett-Packard Corporation (33). These columns have several desirable properties in comparison to glass WCOT columns. In particular, FSOT columns are less fragile and have less polar sites than glass columns. Subsequently, several papers have appeared which show the application of these columns for water analysis (34, 35).

In the latter stages of the experimental phase of this project, two fused silica WCOT columns (30 m x 0.25 mm i.d.) with SE-54 liquid phase were evaluated in conjunction with the LLE method. The following sections describe the application of these columns for the analysis of THMs, volatile organohalides, and certain aromatic compounds. The compounds listed in Table 23 were used in these studies, with the exception of *n*-butylbenzene, *n*-propylbenzene and the two internal standards (i and r). Additionally, *o*-dichlorobenzene (u) and styrene (v) were added in the studies with fused silica columns, and 1,2-dibromoethane (I) was the internal standard in the analysis for THMs.

Fused Silica Capillary GC Analysis of THMs--

Figures 22-23 show chromatograms of the four THMs on the FSOT column using the Hewlett-Packard splitless injection system with the following conditions: 1 μ L injection (Hamilton 7101 syringe); each compound at 2 ng/ μ L; septum purge, 3.3 mL/min.; inlet purge, 72 mL/min.; helium carrier gas, 22 cm/sec. at 0°C; argon/CH₄ makeup to ECD, 49 mL/min.; injector temperature, 100°C; purge vent valve open 0-30 seconds; temperature program, initial temperature, variable (see text); rate, 3°C/min. to end of analysis; ECD attenuation 2×10^7 .

The right-hand trace in Figure 22 shows an isothermal run at 40°C using the splitless mode. At this temperature, a good solvent effect (36) is not observed, since the column temperature is 5° above the boiling point of *n*-pentane. The result is

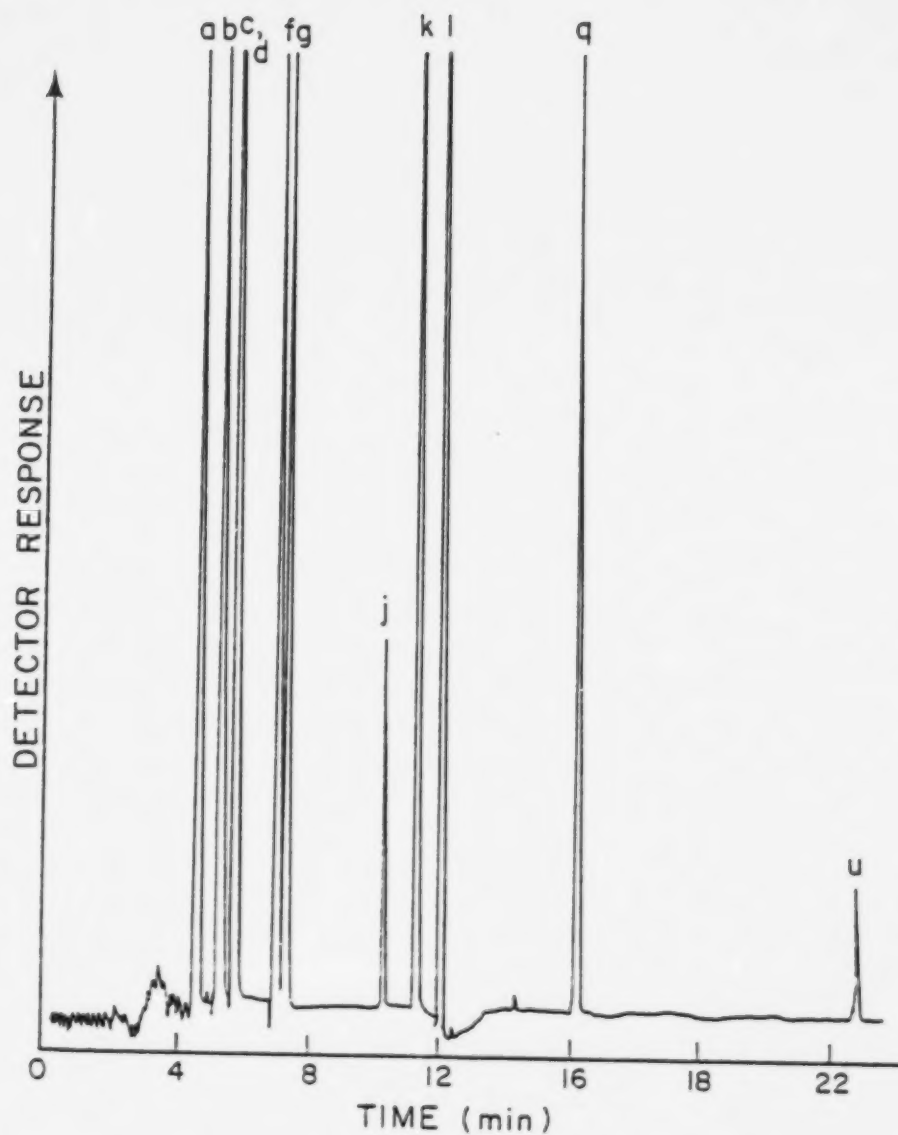


Figure 24. Fused silica capillary column chromatograph (SE-54) of volatile organohalide mixture in *n*-pentane. Initial temperature, 20°C. Other conditions in text; code in Table 23.

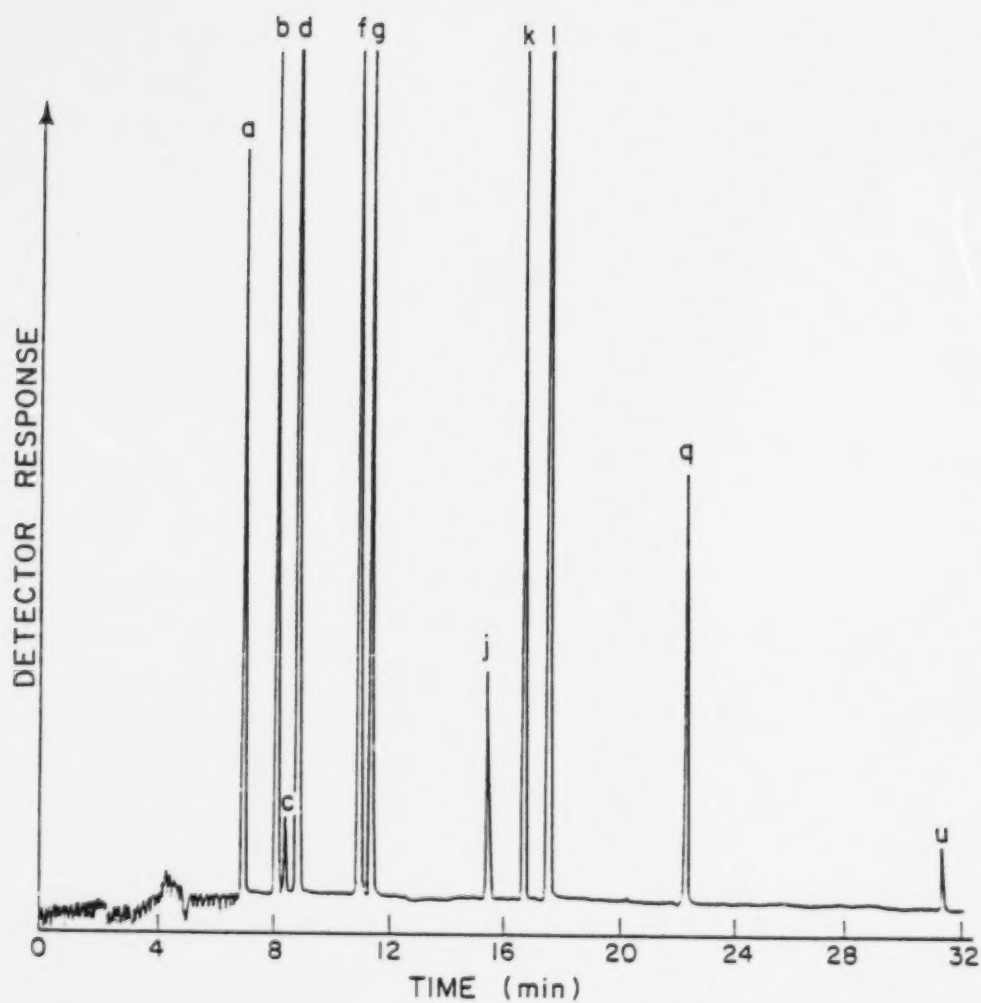


Figure 25. Fused silica capillary column chromatograph (SE-54) of volatile organohalide mixture in *n*-pentane. Initial temperature, 0°C. Other conditions in text; code in Table 23.

TABLE 24. RETENTION TIMES OF ORGANIC COMPOUNDS
ON SE-54 FSOT COLUMN*

Compound	Code	Retention Time	
		Absolute (min)	Relative
<u>Trans</u> -1,2-dichloroethylene*	-	5.08	0.72
Chloroform	a	7.01	1.00
1,1,1-Trichloroethane	b	8.12	1.16
1,2-Dichloroethane	c	8.41	1.20
Carbon Tetrachloride	d	8.84	1.26
Benzene	e	8.96	1.28
Trichloroethylene	f	10.94	1.56
Bromodichloromethane	g	11.39	1.62
1,2-Dibromoethane	i	11.88	1.69
Dichloroacetonitrile	-	12.87	1.84
Toluene	h	15.01	2.14
1,1,2-Trichloroethane	j	15.46	2.21
Chlorodibromoethane	k	16.71	2.38
Tetrachloroethylene	l	17.55	2.50
Ethylbenzene	m	21.00	3.00
<u>p</u> -xylene	n	21.51	3.07
<u>m</u> -xylene	o	21.51	3.07
Bromoform	q	22.31	3.18
<u>o</u> -xylene	p	22.92**	3.27
Styrene	u	22.93**	3.27
Dibromoacetonitrile	-	24.11	3.43
<u>o</u> -Dichlorobenzene	v	31.33	4.47

*20 m x 0.25 mm i.d.; linear helium velocity, 22 cm/sec at 0°C; 1 μ L splitless injection; inlet purge, 72 mL/min; septum purge, 5.3 mL/min; argon/CH₄ to ECD, 49 mL/min; injector temp., 100°; purge vent valve open, 0-30 sec., column temperature program: 0°C, 3 min; 3°C/min to end of run.

** Styrene and o-xylene barely separated; unconfirmed assignments

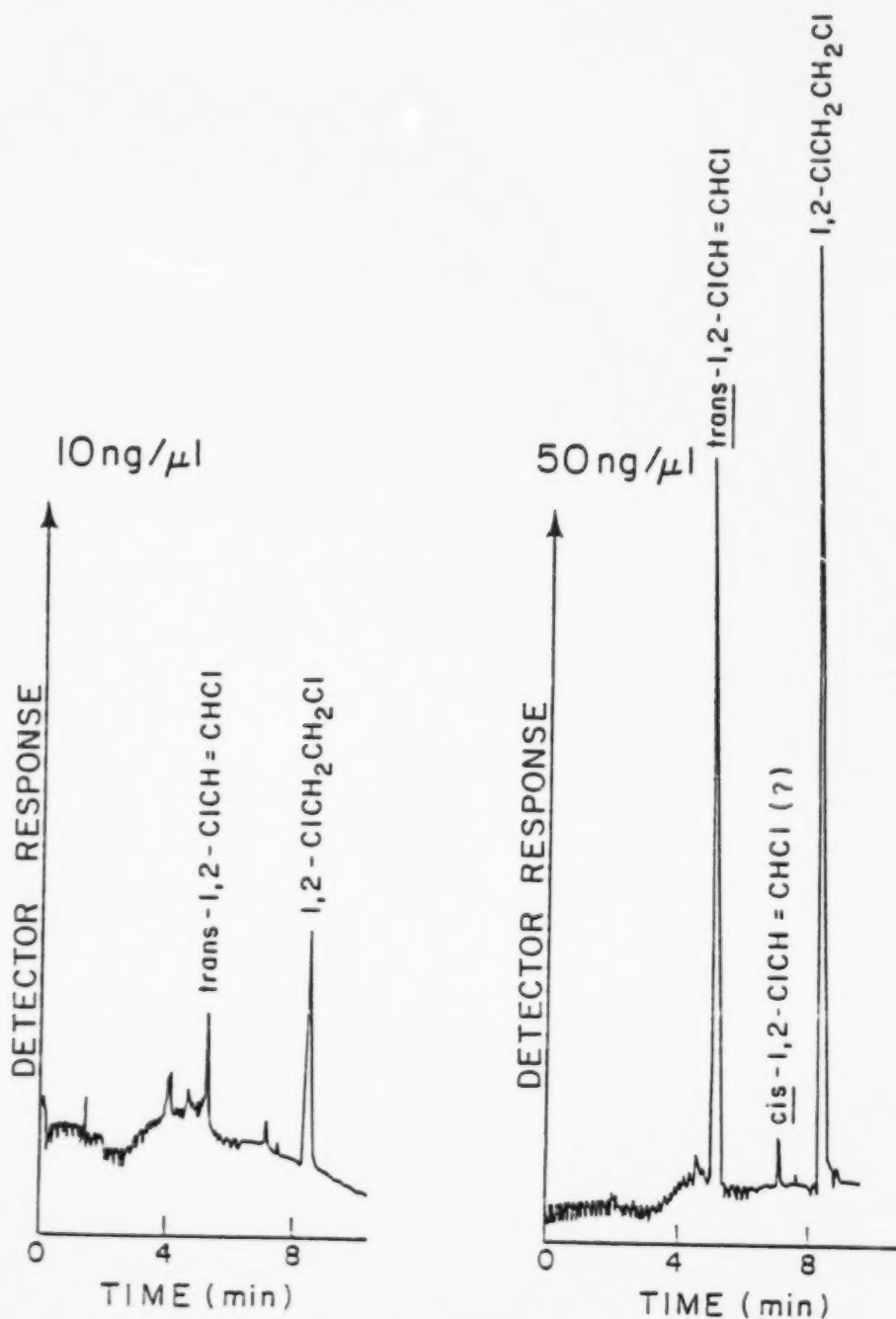


Figure 26. Fused silica capillary chromatograms (SE-54) of two mixtures of commercial grade cis- and trans-1,2-dichloroethene plus 1,2-dichloroethane in n-pentane. Conditions as in Figure 25.

extremely poor resolution. Temperature programming from 40° improves the resolution of the higher boiling peaks, but the chloroform peak shows a ragged frontend characteristic of poor solvent action (left trace in Figure 22).

Figure 23 shows runs under exactly the same conditions except that the initial column temperature is lowered to 30° and 20° respectively. The improvement in the resolution and peak shape is apparent. At the lower initial temperature, THM analysis may be conducted with good precision as experience in this project has shown (see following sections). However, for routine analysis of THMs, little is to be gained by going to capillary columns unless other, more demanding separations are required. Packed column methods would appear to be preferable for the majority of cases where THM monitoring is required.

Fused Silica Capillary GC Analysis of Volatile Organohalides-- Figures 24-25 show chromatograms of a volatile organohalide mixture at the 2 ng/ μ L level for each compound, with the same instrumental settings described in the previous section except that ECD attenuation was 2×10^8 . In Figure 24, the initial column temperature is 20°, and in Figure 25 it is 0°. The critical separation accomplished at the lower temperature is that of 1,1,1-trichloroethane (b), and 1,2-dichloroethane (c). The latter has a much lower EC cross section than the other compounds in the mixture, so its separation is particularly critical. Table 24 lists absolute and relative retention times for the mixture; lower limits of detection of the volatile halides using these GC conditions are discussed in a later section.

Also shown in Table 24 are the retention times of dichloro- and dibromoacetonitrile, two compounds recently reported as found in drinking water supplies (37). These compounds were not included in the majority of this study, but, as noted by Trehly and Bieber, they and the mixed bromo-chloro compound may be analyzed by the LLE/GC technique (38).

Another compound of low EC cross section was investigated briefly. Figure 26 shows FSOT chromatograms of a mixture of trans-1,2-dichloroethylene and 1,2-dichloroethane, run under the conditions described in Figure 25. The identifications were not confirmed by GC/MS and should be taken as tentative. The peak at 6.97 minutes labeled as cis-1,2-dichloroethylene is very speculative since it comes at the same retention time as chloroform. The bottle was labeled cis- and trans-1,2-dichloroethylene, but it is not clear whether both compounds were actually present.

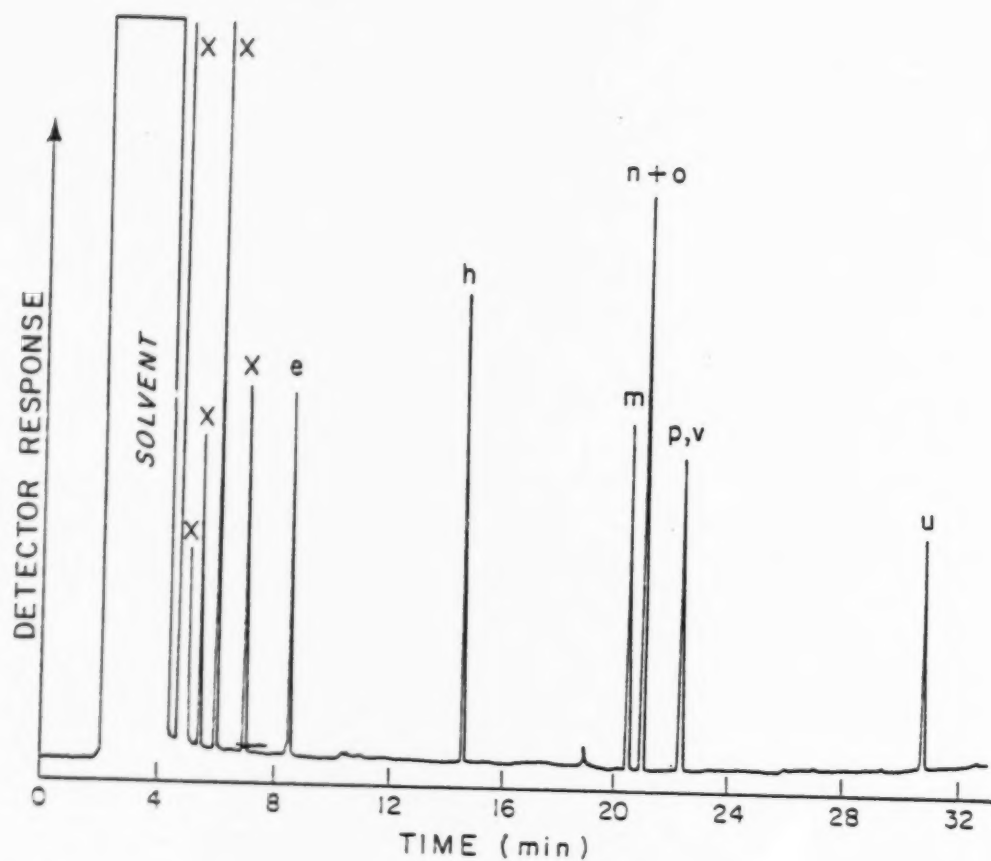


Figure 27. Fused silica capillary column chromatogram (SE-54) of a mixture of aromatic hydrocarbons in *n*-pentane. Conditions same as Figure 16; code in Table 23. Flame ionization attenuation, X2. Concentrations, 2 ng/ μ L.

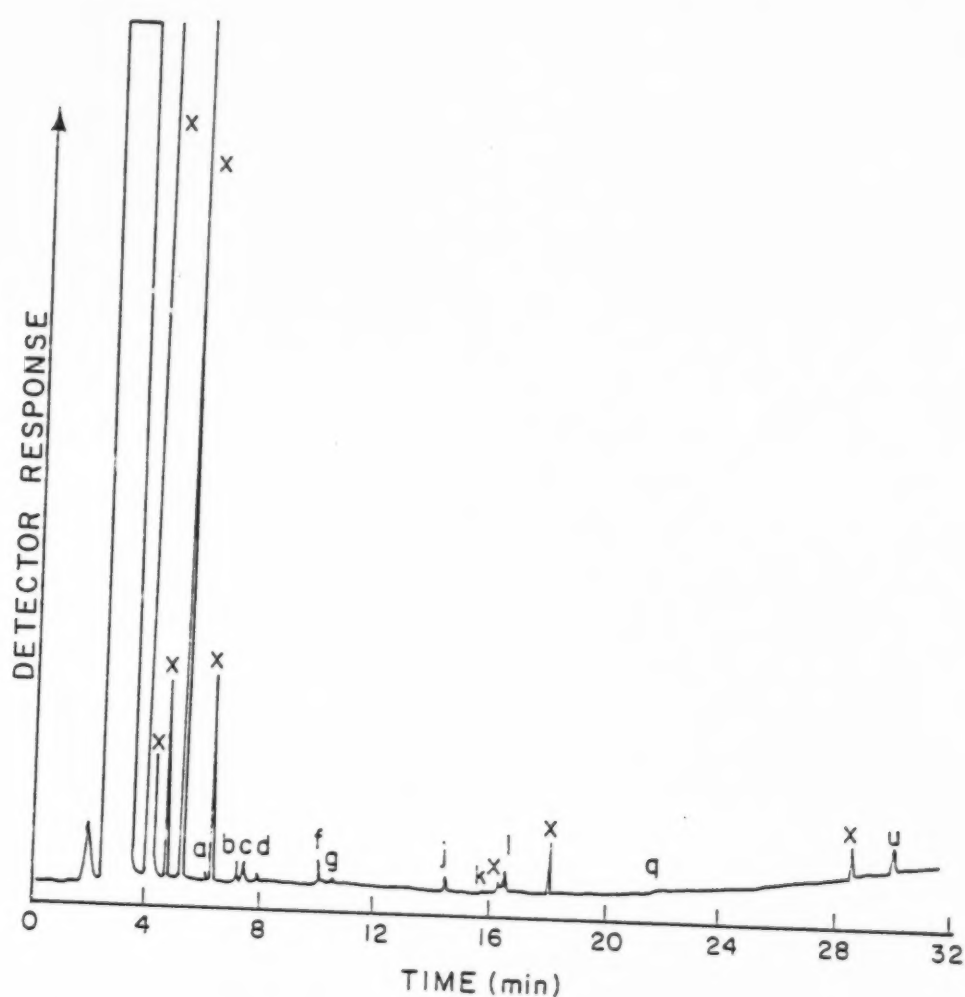


Figure 28. Fused silica capillary column chromatogram (SE-54) of a mixture of volatile organohalides, FID attenuation X2. Code in Table 23; conditions same as Figure 16. Conditions 2 ng/ μ L.

In summary, FSOT columns are capable of the analysis of complex mixtures of volatile organohalides, including those listed in Table 24. For very low boilers such as 1,2-dichloroethylene and vinyl chloride, the FSOT procedure has severe limitations and probably cannot be used in conjunction with the LLE method. Moreover, with splitless injection techniques, cryogenic cooling of the column is necessary which introduces another complicating factor. Liquid carbon dioxide is used in rather large amounts as the cryogenic coolant, adding another costly expense to the procedure. Further discussion of the GC procedure is presented in later parts of this section.

Fused Silica Capillary GC Analysis of Aromatic Hydrocarbons--

The SE-54 columns described above were also used for analysis of aromatic hydrocarbons in *n*-pentane. Figure 27 is a typical chromatogram obtained under the conditions previously described, *i.e.* 0°C for 3 min., 3°C/minutes to end of run.

Two features of this chromatogram are noteworthy, as compared to Figures 21 and 25 respectively. Firstly, the column used in this work has approximately the same separation characteristics as the glass columns shown in Figure 21. In both cases, the liquid phase was SE-54, so it is not surprising the separation is about equal. However, it should be noted that the glass column was twice as long as the FSOT column, 60 m *vs.* 30 m, so resolution per foot appears to be superior with the fused silica column. Note that in Figures 21 and 27, *p*-xylene (*n*) and *m*-xylene (*o*) were not separated.

Secondly, note that the peak widths in Figure 27 are smaller than those in Figure 25. The difference is apparently due to dead volume in the EC detector (Figure 25) compared to FI detector (Figure 27). Figure 28, which shows the FID trace of the same standard as shown in Figure 25, illustrates the difference in response of the organohalides to FI and EC detectors. This is a fortunate circumstance, since mixtures of halides and hydrocarbons may be analyzed by a combination of the two detectors, as discussed before.

Summary of Conclusions Pertaining to GC Conditions

THM Analysis--

For the analysis of THMs by the LLE method using *n*-pentane as the solvent, packed GC columns give satisfactory separation.

A variety of liquid phases may be used to accomplish the separation of THMs, including squalane, SP-1000, SP-2100, etc. For routine work, 10% squalane packed on a suitable support (Supelcoport 100/120 mesh) is recommended. The column should be

glass, with typical dimensions of 9 ft. x 2 mm i.d.

For confirmation purposes, a column of different polarity should be used, such as one containing the SP-1000 phase. Another confirmation column used in this work contained 6% OV-11 and 4% SP-2100.

THM analysis may also be accomplished by capillary column GC. In this work, a fused silica column with SE-54 liquid phase gave excellent resolution, as did a glass SE-54 column and a glass column with a 3:2 mixture of OV-11 and SP-2100. With splitless injection, an initial column temperature of 20°C or lower was required to obtain the good solvent effect required for precise quantification.

For most sensitive analyses, the ECD is recommended for THM analysis, although FID is possible if higher detection limits can be tolerated (see following section).

Volatile Organic Halide Analysis--

Some volatile organic halides may be separated adequately using packed column techniques. Squalane, OV-11, SP-2100 and SP-1000 columns were found to be inferior in this respect to the 6% OV-11/4% SP-2100 mixed phase column. Even with this column resolution was marginal, especially of 1,2-dichloroethane from CCl_4 , and run times are in excess of 30 minutes for CHBr_3 .

Volatile organohalides were separated with greater efficiency using high performance glass or fused silica capillary columns with wall coating. Capillary columns using the Grob-type splitless injection technique, were found to give good resolution and (described later) good precision.

Glass and silica columns with SE-54 wall coating gave adequate separation of the 10 organohalides listed in Table 22. Although not evaluated as thoroughly, the 3:2 OV-11/SP-2100 glass WCOT column appeared to give superior separation as compared to the SE-54 columns.

Again, because of the need for a good solvent effect, n-pentane solutions must be analyzed starting at a column temperature 10-20 degrees below the boiling point of the solvent. For separation of 1,2-dichloroethane from 1,1,1-trichloroethane, an initial temperature of 0° was found to be optimal.

The column temperature regime finally used was 0° for three minutes, followed by an increase of 3°C/minute to the end of the run. Under these conditions, baseline separation of the 10 organohalides was achieved and bromoform eluted at approximately

23 minutes on the 30 m SE-54 FSOT column.

Additional organohalides with retention times in excess of bromoform may also be analyzed by the same procedure, as illustrated by o-dichlorobenzene (31 minutes elution time).

Very volatile organohalides, such as the mono- and dichloroethylenes, are difficult to analyze in n-pentane by the splitless WCOT technique. While not tried in this work, a separate extraction using a more volatile solvent might be successful, albeit not with the splitless injection technique.

The ECD is the detector of choice for organohalides, but for certain compounds the sensitivity is lower than one may require for environmental analyses (see following section).

Aromatic Hydrocarbon Analysis--

Volatile aromatic hydrocarbons such as those listed in Table 22 may be analyzed by the LLE/GC method. In this work, only WCOT columns were used, namely the SE-54 glass and fused silica columns.

Some retention time redundancies were observed with these columns (m- and p-xylene; styrene and o-xylene), but detectability is good with the flame ionization detector. The sharpness of the peaks in this mode indicated that there is less dead volume in the FI as compared to the EC detector.

EVALUATION OF THE HP 7675A PURGE/TRAP MODULE

The Hewlett-Packard (HP) 7675A Purge and Trap Module was used in this work primarily to compare results from the LLE and purge and trap (P/T) methods. In addition, some experiments were carried out to evaluate the module for the analysis of organohalides and aromatic hydrocarbons in water.

The HP 7675A is a compact module which fits directly to the HP 5840 GC, and may be used with either the ECD or FID. The module uses a borosilicate test tube with threaded mouth for the sample purging vessel. Purge gas is introduced through a 1/16" stainless steel tube. The operator may choose settings for pre-purge time; purge time; trap desorption temperature and time; and vent time and temperature. The trap is approximately 8 cm in length and is packed with Tenax with a small quantity of silica gel. Operation is semi-automatic; the operator adds solution to be analyzed to the purge tube and actuates the start button. At the time desorption of the trap begins, the GC program is begun, on this model by a manual procedure. Sample size is usually 5 mL.

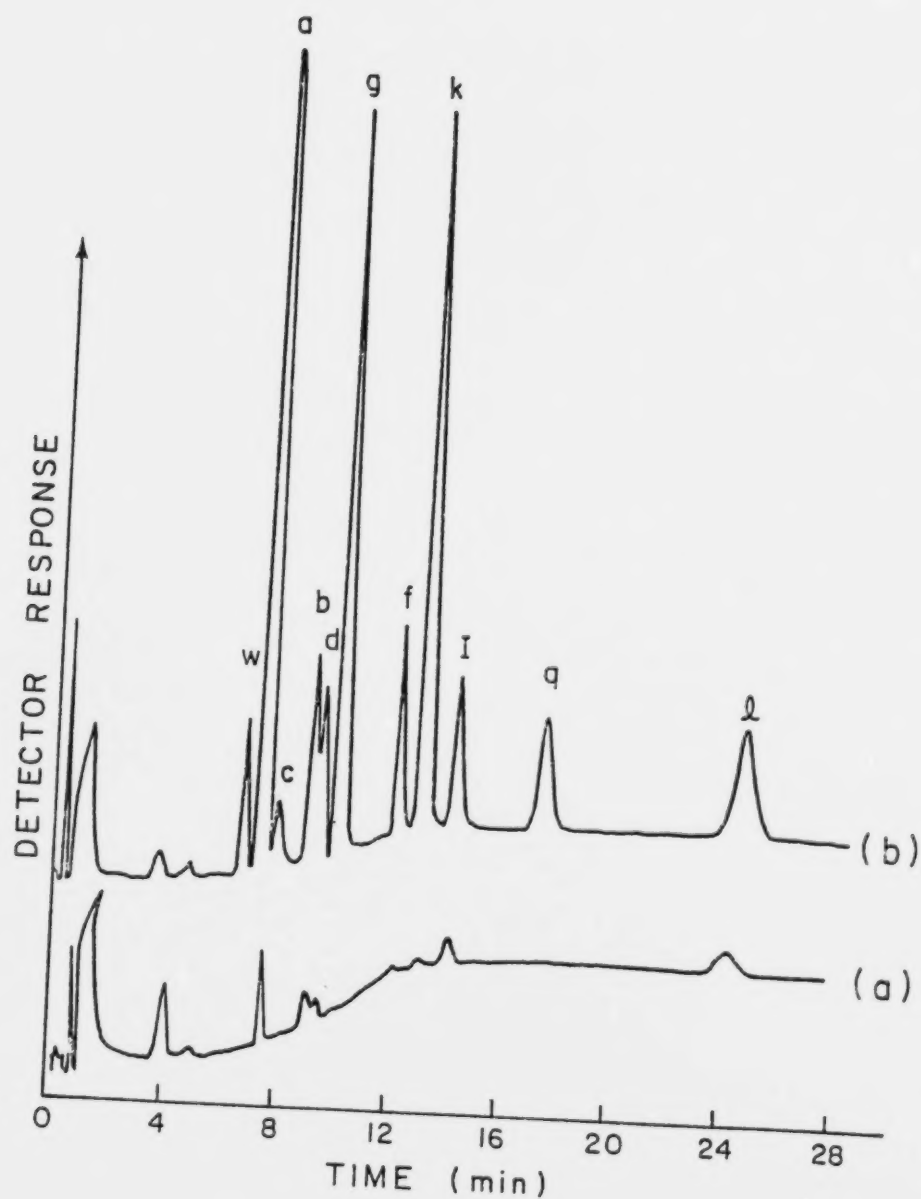


Figure 29. Electron capture purge and trap chromatogram of reagent water (a) and organohalide mixture (b) Hewlett-Packard 7675A purge and trap module with ^{63}Ni ECD. Code in Table 26; conditions in text.

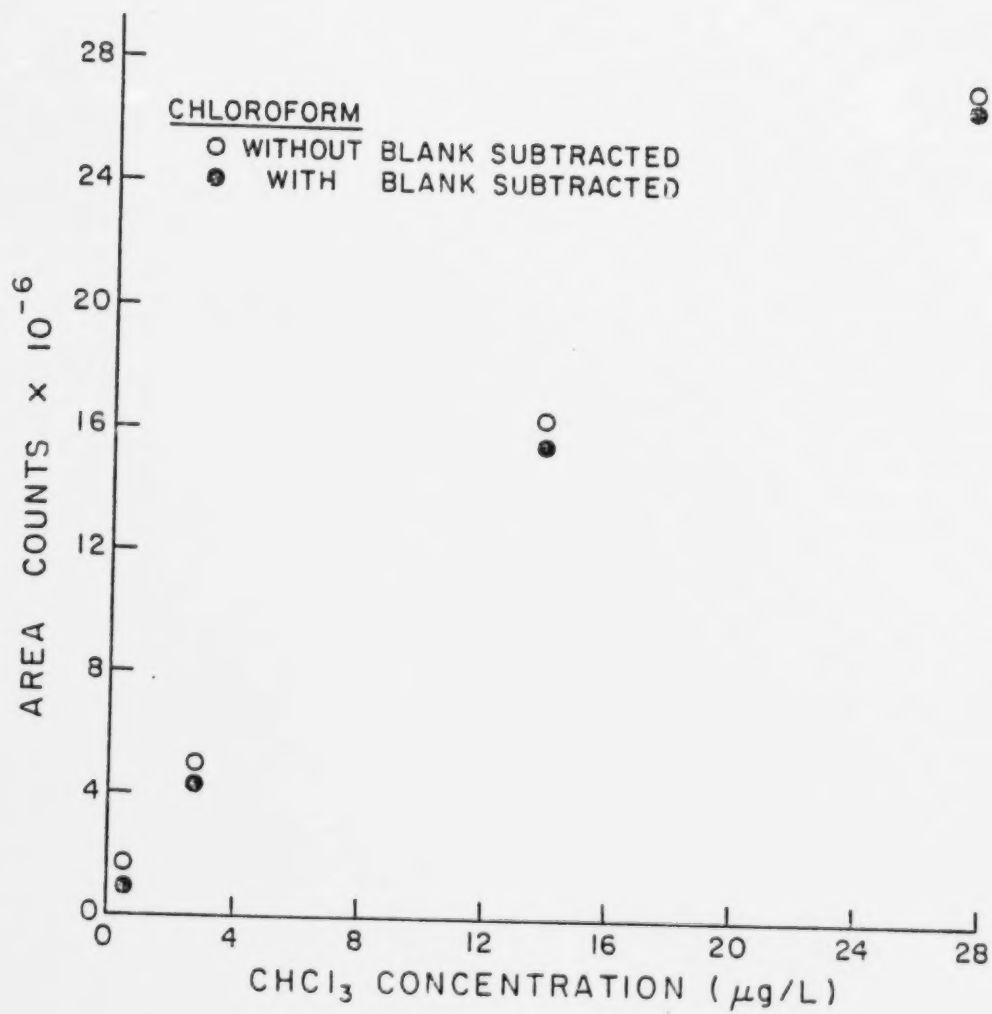


Figure 30. Response of the ECD to chloroform concentrated with the HP 7675A purge and trap module.

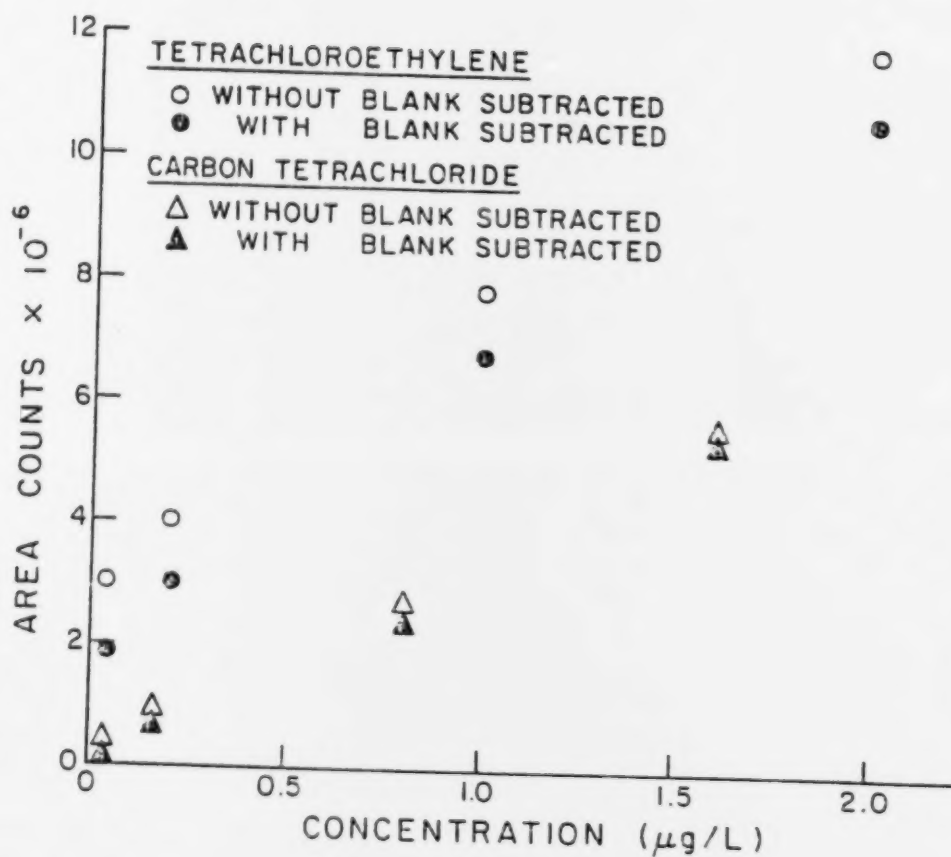


Figure 31. Response of the ECD to tetrachloroethylene and carbon tetrachloride concentrated with the HP 7675A purge and trap module.

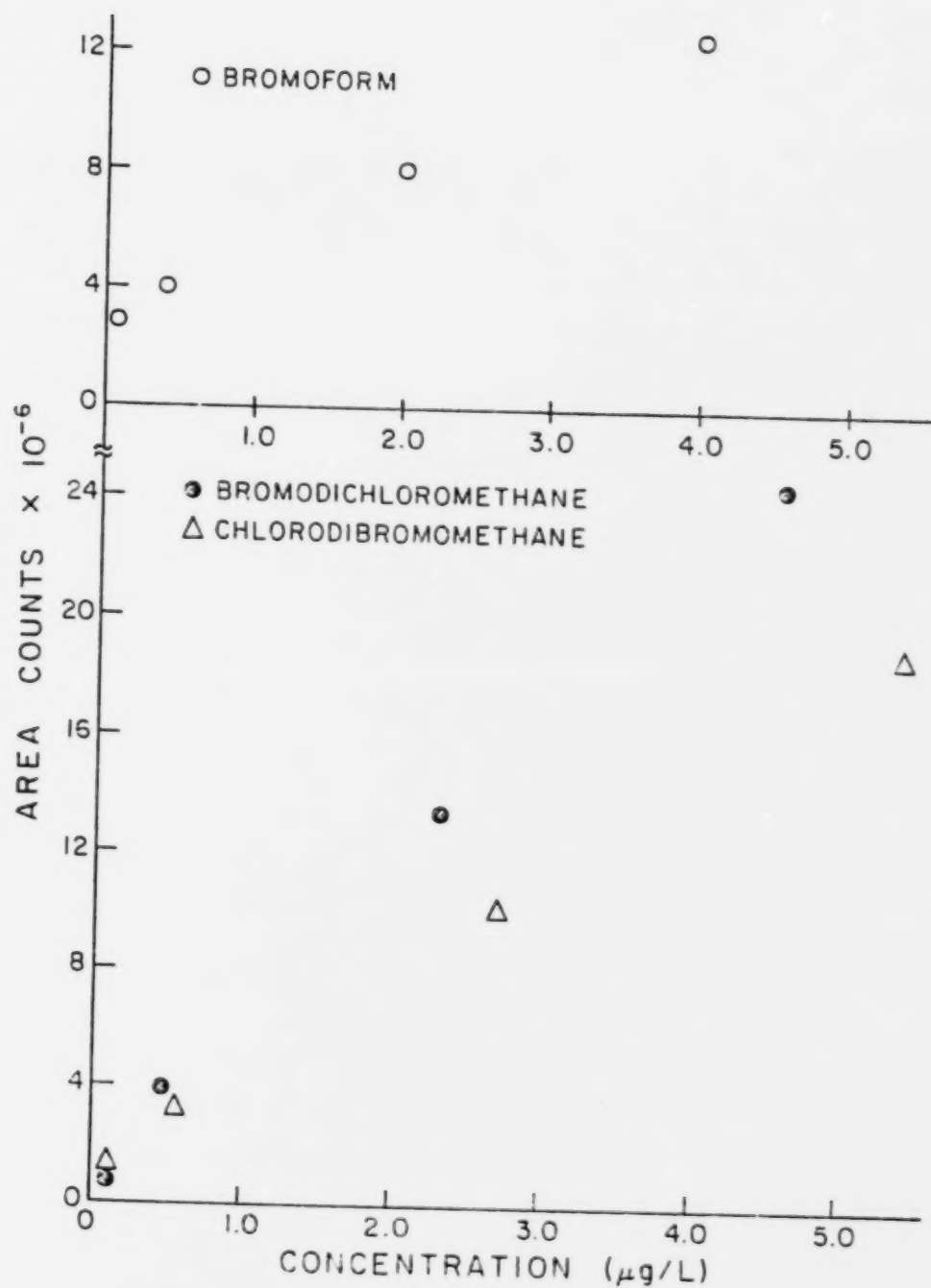


Figure 32. Response of the ECD to bromoform (upper curve) and bromodichloromethane and chlorodibromomethane (lower curve) concentrated with the HP 7675A purge and trap module.

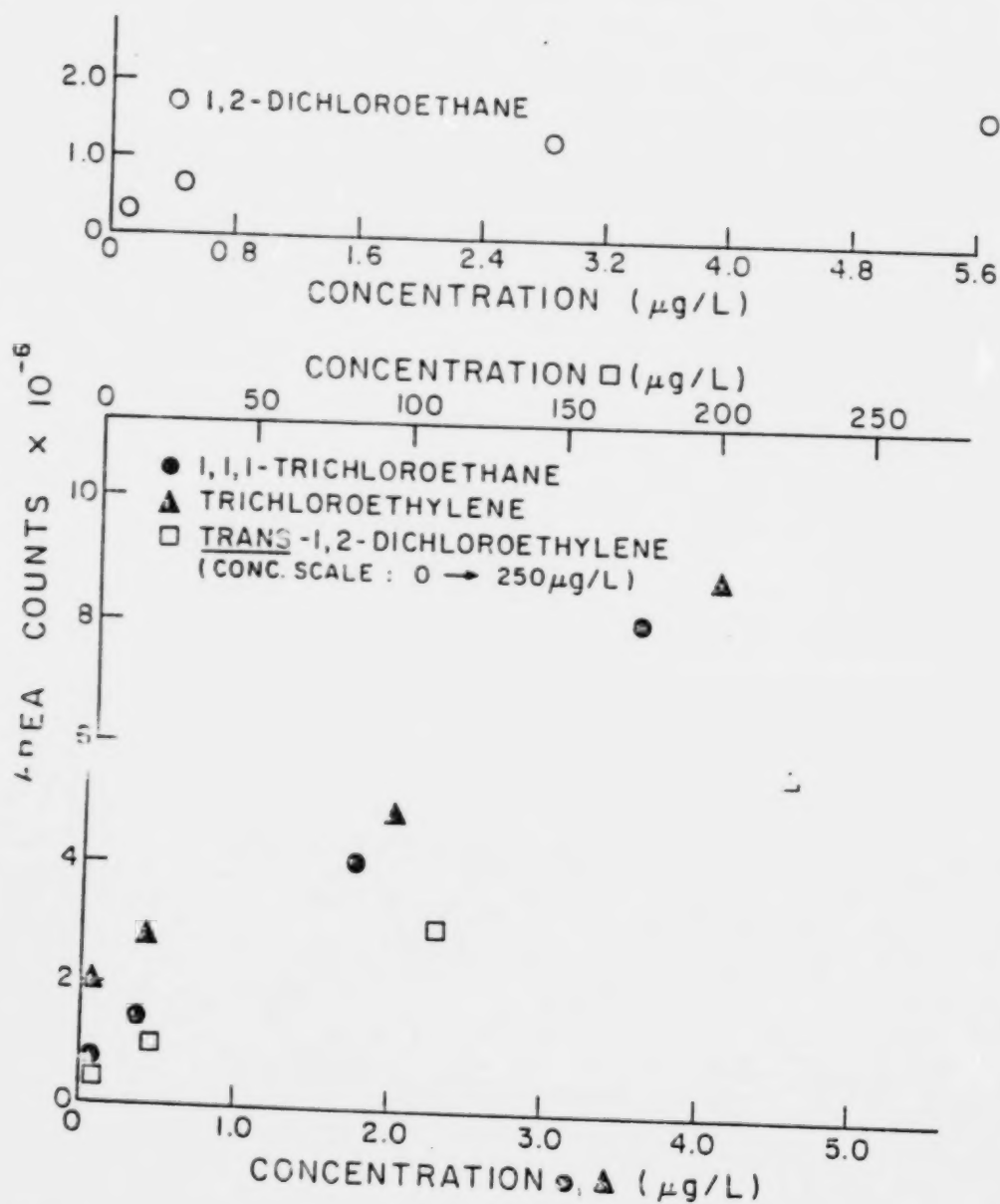


Figure 33. Response of the ECD to 1,2-dichloroethane (upper curve) and 1,1,1-trichloroethane, trichloroethylene, and trans-1,2-dichloroethylene (lower curve) concentrated with the HP 7675A purge and trap module.

Organohalide Analysis with the HP 7675A

The HP 7675A may be used for organohalides either with the ECD or FID. In the former mode, the instrument is highly sensitive, perhaps too sensitive. Figure 29 is an electron capture P/T analysis of a standard mixture labeled as S_c in Table 25*. Note that for most compounds in the mixture, concentrations are below $1 \mu\text{g/L}$, but area counts in excess of one million are the rule.

Such sensitivity is both a blessing and a curse to the analyst. Figure 29a shows laboratory grade (highly purified) water. Concentrations in the water are below $1 \mu\text{g/L}$, but area counts are above 100,000 for several compounds. Thus, the HP 7675A with ECD is capable of very low detection limits. Indeed, in this case the method detection limit is determined not by the sensitivity of the instrument, but by blank levels.

To investigate this matter further, and to determine some information on linearity of the system, four concentrations of the standard shown in Table 25 were investigated, with concentrations of $S_c/5$, S_c , $5S_c$ and $10S_c$. The results are listed in Table 25 as area counts for each of the four solutions. Figures 30-33 are plots of the same data. It is clear that results in the very dilute solution range show evidence of some effect that causes nonlinearity of the plots and/or a nonzero intercept. Figure 30 is a plot of chloroform data with and without correction for CHCl_3 in blanks. Here the nonzero intercept is largely eliminated, but curvature in the plot remains. In Figure 31 blanks are subtracted from data for tetrachloroethylene and carbon tetrachloride with good effects in the latter but not the former case.

Apparently, several effects may be contributing to the nonzero intercepts and nonlinear calibration plots shown in the figures. At integrator counts above 10^7 there is the danger of saturation of the ECD. Samples may be diluted to concentrations low enough to avoid this problem, but contamination with laboratory water constituents is then a potential problem. If concentrations become too low (i.e. below $0.1 \mu\text{g/L}$) one also must be concerned about losses due to adsorption and decomposition.

* In Figure 29, the standard mixture contains $0.50 \mu\text{g/L}$ of 1,1,2-trichloroethane which elutes with CHBr_2Cl at 13.42 minutes.

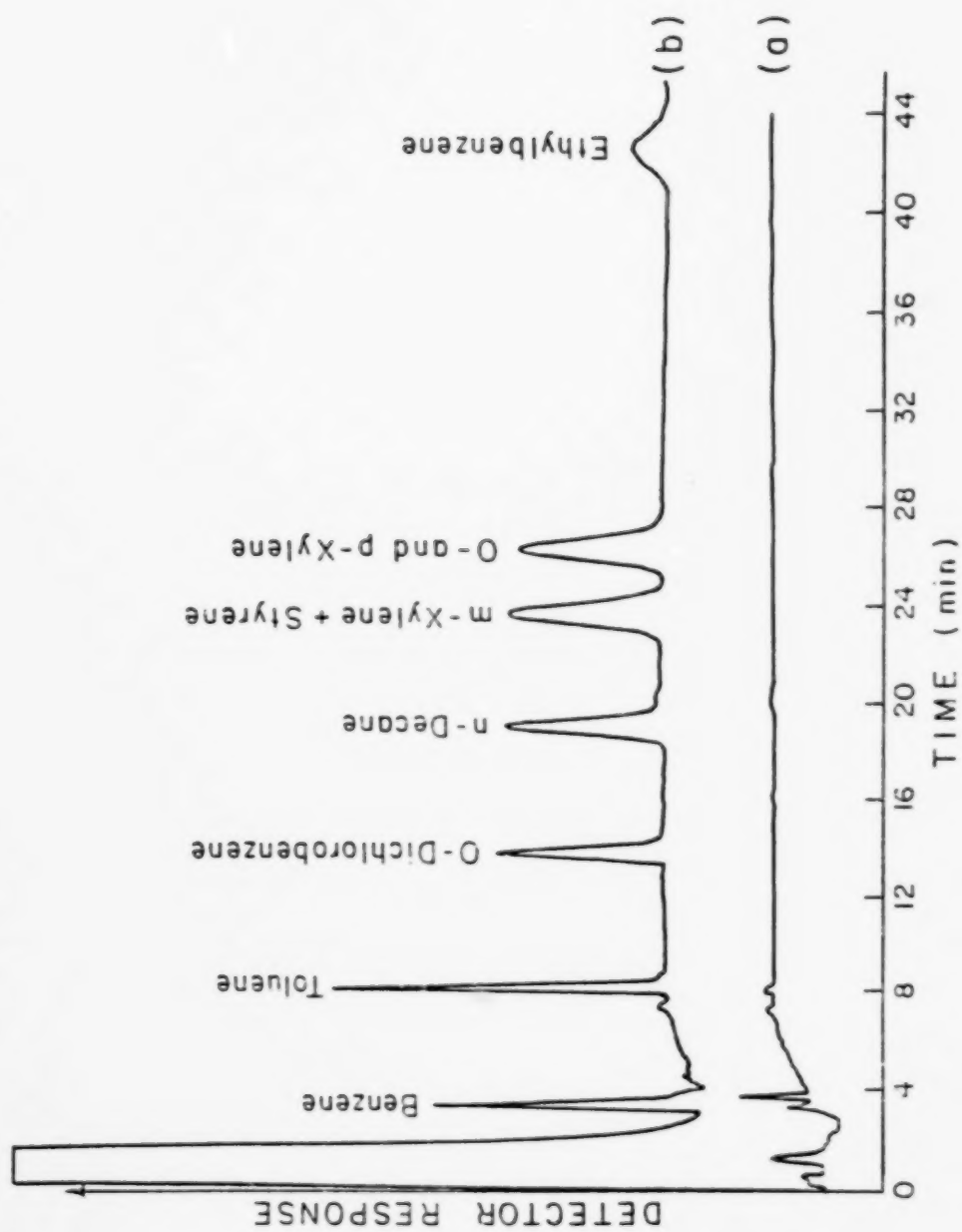


Figure 34. Flame ionization, purge and trap chromatogram with HP 7675A module (a) water blank; (b) standard mixture (Table 27).

For example, consider the analysis of a water sample for tetrachloroethylene (PCE). Figure 31 shows that one is advised to obtain integrator counts between 5×10^6 and 15×10^6 , corresponding to 1 and 16 ng respectively. In an undiluted 5 mL sample these correspond to PCE concentrations of 200 ppt (ng/L) and 3.8 ppb ($\mu\text{g/L}$) respectively. Below this range adsorption and/or decomposition losses may occur, and above it the detector shows evidence of becoming nonlinear.

Table 25 gives a recommended range for area counts of each compound, which may be considered to be the working range of the purge and trap - ECD method for organohalides.

Other matters of interest with regard to the analysis of organohalides with the HP 7675A are: (a) GC resolution; and (b) precision. The former was not evaluated carefully, but it appears the unit, in combination with the HP 5840A chromatograph is capable of resolution comparable to what one obtains with other purge and trap apparatus (1).

Precision of the method is illustrated by the data in Table 25, particularly for standard samples at concentrations S_c and $5S_c$, which are generally in the recommended working range of the method.

Finally, it should be noted that evidence discussed in a following part of this section suggests that a GC artifact is responsible for the response curve shown in Figure 33 for 1,2-dichloroethane.

Aromatic Hydrocarbon Analysis with the HP 7675A

Figure 34 is a chromatogram of an eight-compound standard of aromatic hydrocarbons plus *n*-nonane which may serve as an internal standard. The column was the same as the one used for purge and trap analysis of organohalides, not necessarily the column of choice for hydrocarbons. However, the column was evaluated in order to determine if simple aromatics, particularly benzene and toluene, could be measured precisely. As Table 26 and Figure 34 show, the method is reproducible within 10-15% for the compounds evaluated, but resolution is poor. If purge and trap - FID is to be used for hydrocarbon analysis, a better column can surely be found which will improve separation and shorten analysis time.

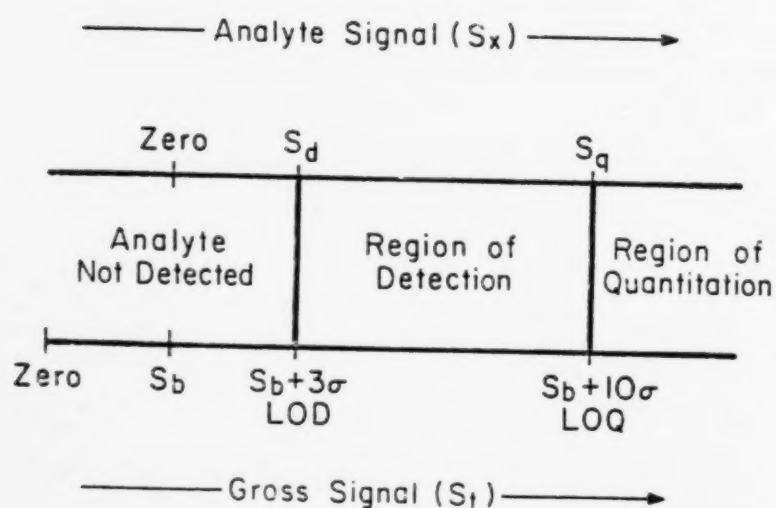


Figure 35. Schematic diagram showing regions of detection and quantitation of an analytical method. LOQ = limit of quantitation; LOD = limit of detection (method detection limit, MDL), S_b = signal level in blank; σ = standard deviation of blank [from "Data Acquisition and Data Quality Evaluation in Environmental Chemistry", Amer. Chem. Soc. (22)].

TABLE 25. PURGE AND TRAP ANALYSIS OF ORGANOHALIDES WITH THE HP 7675A MODULE^a

COMPOUND	Code	Retention Time (min)	Standard Mixture ^b Sc (µg/L)	Area Counts $\times 10^{-6}$ (Std. Dev.)			Response (Area/ng)	Recommended Range (10 ⁶ Area Cts)	Blank (Area Cts $\times 10^{-6}$) ^d
				Sc/5	Sc	5Sc			
Trans-1,2-dichloroethene	w	7.04	22.8	0.42 (0.09)	0.93 (0.10)	2.96 (0.49)	0.005	0.5-6	0.06
Chloroform	a	7.73	2.76	1.52 (0.06)	4.97 (0.55)	16.13 (2.32)	0.18	4-30	0.61
1,2-Dichloroethane	c	8.28	0.57	0.34 (0.04)	0.64 (0.07)	1.28 (0.12)	0.05	>20	0.10
1,1,1-Trichloroethane	b	9.46	0.35	0.74 (0.06)	1.45 (0.15)	4.12 (0.66)	0.43	2-10	0.46
Carbon Tetrachloride	d	9.79	0.16	0.36 (0.02)	0.93 (0.22)	2.71 (0.38)	0.69	1-7	0.28
Bromodichloromethane	g	10.45	0.46	1.26 (0.06)	3.93 (0.45)	13.26 (1.80)	1.00	4-25	0.31
Trichloroethylene	f	12.55	0.40	2.17 (0.12)	2.69 (0.58)	4.88 (0.73)	0.33	2-10	0.45
Chlorodibromomethane	k	13.42	0.54	2.12 (0.03)	5.28 (0.62)	15.98 (1.76)	0.65	4-20	0.43
1,2-Dibromomethane	i	14.63	0.28	-	-	-	-	-	-
Bromoform	g	17.77	0.40	2.94 (0.26)	3.38 (1.35)	7.97 (0.52)	0.50	5-10	0.19
Tetrachloroethylene	l	24.95	0.20	2.99 (0.53)	3.81 (0.95)	7.05 (1.41)	0.95	5-15	1.07

a. 10 min He purge at 40 mL/min; desorb 250°; 0.2% Carbowax 1500 Carbopac C (80/100); 60°, 3 min, 8°/min to 130°;
b. Figure (40);
c. N = 3,9,3,1 for Sc/5, Sc, 5Sc and 10Sc respectively;
d. Blank consisted of internal standard plus reagent water.

DETECTION LIMITS OF THE 20:1 AND 240:1 LLE METHOD--THMs,
ORGANOHALIDES, AND AROMATIC HYDROCARBONS

Definition of Terms Associated with Detection Limits

Detection limit is a term used to refer to the lowest level of an analyte which can be measured with confidence. Method detection limit (MDL) refers to the lowest level measurable with confidence for a complete analytical procedure (40-42). In the case of the LLE method, this refers to the sampling procedure, extraction step, and GC analysis (including calibration). Instrument detection limit refers only to the GC analysis, i.e. the analysis of organohalides and aromatics in pentane using a specified GC procedure. Sensitivity is defined as the ratio of change of the instrument response to the change in analyte concentration.

Instrument detection limit is determined primarily by the response of the GC detector toward the analyte, and by factors associated with the injection/separation process. For example, detection limits of capillary GC analysis using the split mode are usually different than with splitless procedures.

In general, instrument detection limits are lower than MDLs, but both are affected by the quality of reagents used. Thus, contaminants in the pentane solvent may elute from the GC at the same retention time as analytes, raising the net instrument detection limit. This was the case for chloroform, found to be present in essentially all pentane lots available from commercial sources. MDLs are subject to purity of the solvent as well, but also to the purity of glassware used for the extraction, the purity of water used to prepare calibration standards, and to other random errors associated with the analytical procedure.

Method Detection Limit (MDL) or (Limit of Detection, LOD), often has been defined as the level of analyte which can be observed reliably with a signal to noise (S/N) ratio of 3 (22). Crude estimates of DL have been made by analyzing a solution near the detection limit, and estimating the level which would give a S/N level of 3. An extension of this procedure is described by an American Chemical Society Committee on Environmental Improvement report (22) in which detection limits are discussed in terms of the relationship between gross analyte signal S_t , the field blank S_b , and the variability of the blank σ_b . The limit of detection is defined by the extent to which S_t exceeds S_b ; usually MDL is located 3 above S_b . This is illustrated in Figure 35 where the bottom scale is the gross signal S_t and the top scale is the net signal $S_x = S_t - S_b$.

Following this concept, the procedure for determining the MDL of an analyte would be to determine the standard deviation of field blanks, and to then calculate the MDL from the relationship

$$MDL = S_d/a = (S_b + 3\sigma)/a$$

where a is a proportionality constant converting from the units of detector signal to concentration units.

The Limit of Quantitation is a more conservative detection limit, being 10 above the field blank mean. Above this level, there are presumably lower risks of false positives (39).

Recently, Glaser et al. have described a pragmatic method for determining detection limits (40, 41). MDL is defined as "the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of a sample of a given matrix containing analyte. A minimum of seven replicate samples are processed through the analytical scheme and the value of analyte determined in each case. The MDL is computed as:

$$MDL = t_{(N-1, 1-\alpha = .99)} \times \sigma_c$$

where σ_c is the relative standard deviation of the replicates and $t_{(N-1, 1-\alpha = .99)}$ is the student's t value for a one-tailed test at the 99% confidence level with $N-1$ degrees of freedom.

Results

Two separate sets of studies were carried out to determine detection limits for the LLE method. One was for THMs and other organohalides using packed column GC methods and a commercial instrument with ECD. In the second approach, the same instrument and detector were used with capillary columns to investigate detection limits for organohalides and aromatic hydrocarbons. In both studies, the 20:1 pentane method was utilized, as described in the Experimental Section and in the following part of this section.

Packed Column GC/EC Detection Limits--

In the first study, a packed column with 6% OV-11/4% SP-2100 on 100/120 Supelcoport was used, and both method and instrument detection limits were determined. Instrument detection limit was determined using pentane solutions of the individual organohalides near the detection limit. GC/EC traces were obtained at an attenuation of 2^6 and the peak heights of the analytes (S) were measured against the baseline to peak noise

TABLE 26. PURGE AND TRAP ANALYSIS OF AROMATIC HYDROCARBONS WITH THE HP 7675A MODULE^a

COMPOUND	Code	Retention time (min)	Calibration Standard (µg/L)	Precision ^b (%S.D.)	Response ^c (Area Cts) ng	Detection ^d Limit (µg/L, Est)
Benzene	e	3.91	3.1	9	5.0	16
Toluene	h	8.68	4.4	9	3.2	32
o-Dichlorobenzene	u	14.2	4.8	10	2.6	39
n-Octane	IH	19.5	5.6	-	3.8	-
m-Xylene	o)	24.1	7.1	7	3.5	23
Styrene	v)					
o-Xylene	m)					
p-Xylene	p)	26	8.2	5	3.0	26
Ethylbenzene	m	43.0	3.1	10	3.1	19

a; 6 ft x 2 mm i.d. glass column with 0.2% Carbowax 1500 on 80/100 Carpopack C, 130°, 3 min; 15°/min to 160°; trap desorb at 250°, 5 min.; purge 10 min at 40 mL/min (helium),

b; quadruplicate analyses,

c; at concentrations listed; area counts x 10⁻²

d; see following section

TABLE 27. SIGNAL/NOISE ESTIMATION OF LLE DETECTION LIMITS BY ECD^a

COMPOUND	Instrument Detection ^b Limit (pg/ μ L)	Instrumental Method Detection ^c Limit (μ g/L)
Chloroform	2.1	0.10
1,1,1-Trichloroethane	0.90	0.05
Carbon Tetrachloride	0.33	0.02
1,2-Dichloroethane	116	5.8
Trichloroethylene	2.7	0.14
Bromodichloromethane	1.0	0.05
Tetrachloroethylene	1.4	0.07
Dibromochloromethane	2.1	0.10
Bromoform	6.9	0.34

^a

Determined with the mixed phase column on the HP 5840A at an attenuation of 2^6 . The peak to peak high frequency noise was converted into a peak height equivalent to a S/N of three.

^b

Detection limit based upon actual concentration in pentane extract with 2 μ L injection.

^c

Instrument detection limit divided by the concentration factor of twenty.

TABLE 28. LLE METHOD DETECTION LIMITS DETERMINED BY REAGENT BLANK WITH ECD^a

COMPOUND	Concentration in Blank ^b (µg/L)		Method Detection Limit (µg/L)	
			Qual. ^c	Quant. ^d
Chloroform	0.225	0.459		
	0.302	0.444	0.43	2.2
	0.310		0.49	0.65
Mean	0.279±0.050	0.451±0.013	0.46	1.4
1,1,1-Trichloroethane	0.041	0.062		
	0.028	0.056	0.059	0.16
	0.036		0.074	0.13
Mean	0.035±0.008	0.059±0.005	0.067	0.15
Carbon Tetrachloride	0.012			
	0.011			
	0.011			
Mean	0.011±0.0009		0.014	0.025
Tetrachloroethylene	0.443	0.258		
	0.353	0.279	0.59	3.0
	0.451		0.33	0.55
Mean	0.416±0.058	0.269±0.019	0.46	1.8

^a Detection limits of the LLE Method determined by reagent contaminants; HP 5840A with mixed phase column at attenuation of 2⁸ with 2 µL injection.

^b Reagent water, pentane, and internal standard.

^c Mean blank +3 standard deviations; Limit of Detection

^d Mean blank +15 standard deviations; Limit of Quantitation

level (N). The concentration of analyte (picograms/ μ L) required to give a S/N ratio of 3 was then calculated, assuming the response was linear over the range of the extrapolation. These are listed in Table 27 along with values of what we shall define as the instrumental method detection limit (μ g/L). The latter is the instrument detection limit converted into a theoretical value in a water sample, assuming 100% extraction efficiency at a 20:1 ratio of water:pentane. For example, the instrument detection limit for trichloroethylene in pentane was 2.7 pg/ μ L from noise measurements. However, due to the concentration factor of 20, this corresponds to an instrumental method detection limit in water of 0.14 μ g/L. That the actual extraction efficiencies are below 100% is irrelevant to these calculations, since instrument detection limits are of no pragmatic significance.

MDLs for the 20:1 pentane LLE method were estimated using reagent blanks and the same GC procedure described above, except that the ECD attenuation level was 2⁸. In this series of experiments, Baker Resi-analyzed pentane, lot 736992, was used with the regular 20:1 LLE procedure to extract two different lots of reagent water on different days. The water was extracted in duplicate or triplicate, and the pentane extracts were analyzed vs. aqueous standards. The average reagent blank contaminant levels and their standard deviations were determined on the two lots of reagent water. These contaminants include contributions from the pentane, the internal standard (1,2-dibromoethane), and the reagent water. The results are collected in Table 28.

Four of the nine compounds were detected in the reagent blanks--chloroform, 1,1,1-trichloroethane, carbon tetrachloride, and tetrachloroethylene. The qualitative MDLs are defined as the average blank concentrations plus three standard deviations of the blank, i.e. 99.6% confidence limits above the blank. These values should be greater than the corresponding instrument method detection limits listed in Table 27. Examination of the mean blank concentrations showed that carbon tetrachloride in the blank was near the instrument detection limit. This was verified by the blank analysis run on the second lot of water where no carbon tetrachloride was detected, although the other contaminants were found. Also shown in Table 28 are quantitative detection limits which were arbitrarily defined as the reagent blank mean plus 15 standard deviations. Qualitative and quantitative detection limits are terms analogous to Limit of Detection and Limit of Quantitation in the ACS nomenclature (22). Table 28 is particularly instructive as regards the difference between instrument detection limit and an MDL for a substance such as chloroform. Chloroform is found almost ubiquitously in blanks and the Limit of Quantitation of the LLE method is therefore no lower than one to two μ g/L. This is a factor of

TABLE 29. MDLs BY CAPILLARY GC/LLE METHOD^a ORGANOHALIDES ($\mu\text{g/L}$)

COMPOUND	Standard No. I				Standard No. II			
	$\bar{X}$	σ	N	MDL	$\bar{X}$	σ	n	MDL
Chloroform	2.53	0.18	7	0.57	5.36	0.95	8	2.9
1,1,1-Trichloroethane	0.32	0.05	7	0.16	0.74	0.21	9	0.6
1,2-Dichloroethane ^b	0.53	0.05	7	(0.16) ^b	1.24	0.15	9	(0.4) ^b
Carbon Tetrachloride	0.16	0.05	7	0.15	0.37	0.10	10	0.3
Trichloroethylene	0.39	0.09	6	0.30	0.82	0.21	10	0.6
Bromodichloromethane	0.47	0.03	6	0.11	1.08	0.21	9	0.6
1,1,2-Trichloroethane ^c	nm	nm	-	-	1.19	0.22	9	0.6
Chlorodibromomethane	0.59	0.05	5	0.2	1.37	0.26	9	0.8
Tetrachloroethylene	0.18	0.08	6	0.3	0.47	0.07	9	0.2
Bromoform	0.53	0.13	7	0.4	0.98	0.20	9	0.6
1,2-Dichlorobenzene ^c	nm	nm	-	-	10.0	0.48	4	2.2

^a20:1 pentane method with SE-54 FSOT capillary GC analysis; see text for details

^bsee text for further discussion

^cnm: not measurable

TABLE 30. MDLs BY CAPILLARY GC/LLE^a AROMATICS (ug/L)

COMPOUND	$\bar{X}$	σ	n	MDL
Benzene	23.4	4.7	6	16
Toluene	45.3	9.6	6	32
Ethylbenzene	25.2	5.7	6	19
p-Xylene)	87.0	13.3	6	23 ^b
m-Xylene)				
x-Xylene)	69.4	15.4	6	26 ^b
Styrene)				
1,2-Dichlorobenzene	42.3	11.6	6	39

a. 20:1 pentane method with SE-54 FSOT capillary GC analysis;
see text for details.

b. Based on either compound that co-elute.

TABLE 31. 120:0.5 LLE METHOD: ESTIMATED DETECTION LIMITS
(CAPILLARY COLUMN GC METHOD)

COMPOUND	MDL ($\mu\text{g/L}$) ^a	
	FID	EC
Chloroform	14	0.16
1,1,1-Trichloroethane	5	0.10
1,2-Dichloroethane	8	2.2
Carbon tetrachloride	b	0.005
Benzene	1	b
Trichloroethylene	6	0.03
Bromodichloromethane	8	0.06
Toluene	0.9	b
1,Chloro-2-bromopropane	c	c
1,1,2-Trichloroethane	d	d
Chlorodibromomethane	9	b
Tetrachloroethylene	4	0.04
Ethylbenzene	0.6	b
p-Xylene	0.6	b
m-Xylene	0.6	b
o-Xylene	0.6	b
Bromoform	14	0.09
1,4-Dichlorobutane	c	c
n-Propylbenzene	0.8	b
n-Butylbenzene	0.8	b

^aReference capillary column chromatograms in Figures 20 and 21.

^bNot measured, but large.

^cInternal standard.

^dValues not known.

approximately 10-20 times the instrument detection limit.

Capillary Column Detection Limits--

A much more thorough study of the 20:1 pentane LLE method was carried out using the EPA procedure described by Glaser et al. (40, 41). In this study, the same extraction procedure was used (see Experimental Section and next part of this section), but the analysis was done with an SE-54 FSOT capillary column. The splitless injection module of the HP 5840A was utilized as described in the Experimental Section. The temperature program was 0°C, 3 minutes, 3°C/minute to end of program. A 0.50 minute purge delay and 1.0 µL injections were employed. Aromatics and organohalides were detected with FID and ECD respectively. Standards were prepared in replicates using the best water available.

The results are shown in Table 29 and 30 for organohalides and aromatics respectively. For organohalides, two concentrations are shown, one about twice the concentration of the other. In general, the solution of higher concentration gave higher MDL values, but it is not clear why this is the case. Nonetheless, the larger values are used as the MDLs of the organohalides. Note that in every case except tetrachloroethylene, the MDL values obtained by the EPA method are larger than those given in Tables 27 and 28. Tetrachloroethylene may be exceptional due to unusually high blanks observed in the earlier studies (Table 28). For tetrachloroethylene, an MDL of 0.2 is assumed to be correct.

Two solutions of aromatic compounds were also prepared but one, having about one-fifth the concentration levels shown in Table 30, was too low to measure by the GC integrator. MDL values were calculated by the EPA procedure (40, 41) and the results are shown in Table 30.

Detection Limits of the 240:1 LLE Method--

The 240:1 method utilizes a 120-mL serum bottle with 1 mL of water removed and 0.5 mL pentane added. Mixing is facilitated by sonication and extraction efficiencies are enhanced by addition of 5 grams of NaCl (see Experimental Section). This method is recommended only when very low levels of analytes are being analyzed. Table 31 gives approximate detection limits based on the signal/noise procedure described above using a spiked drinking water matrix. In general, the values in Table 31 are somewhat lower than one would expect based on Table 30. It should be emphasized that the values for the 240:1 LLE method are only approximate.

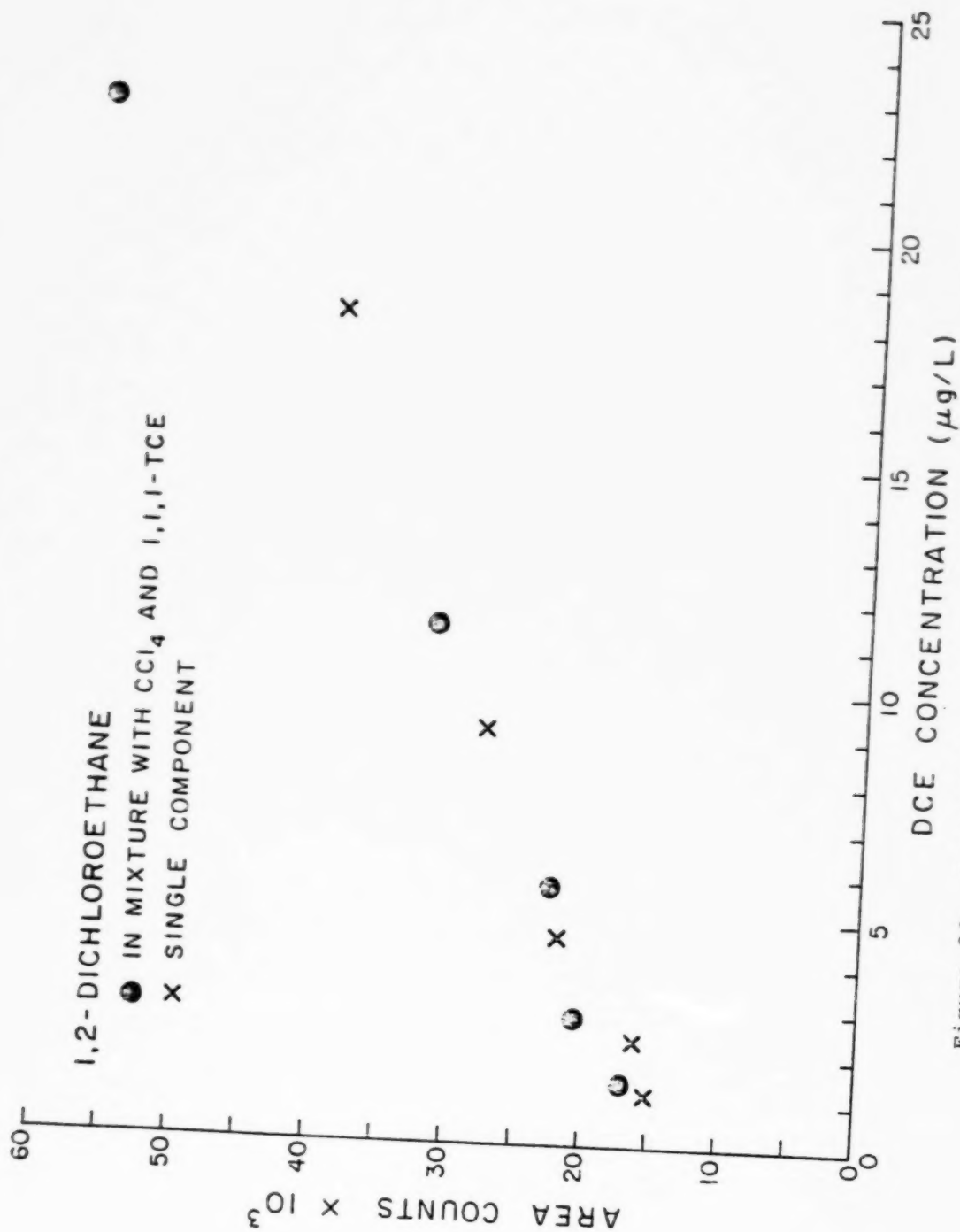


Figure 36. Sensitivity plot for GC analysis of 1,2-dichloroethane in pentane (GC conditions as in Figure 25).

Detection Limit for 1,2-Dichloroethane--

Of the compounds currently under most active consideration as possible contaminants in drinking water (2), two cannot conveniently be determined by the LLE method: vinyl chloride and 1,2-dichloroethane (DCE). The former is too volatile and not easily separated by GC in a pentane solution. The latter has a low electron capture cross section and therefore a high detection limit. In Table 27, the packed column/GC instrument detection limit translated to a water solution is approximately 6 $\mu\text{g/L}$. In Table 29, however, an MDL of 0.4 $\mu\text{g/L}$ is estimated, and indeed a solution of 0.53 $\mu\text{g/L}$ nominal concentration gave an observable signal at the DCE retention time. Since earlier work had shown that such a low concentration could not be detected, further study of this compound was carried out.

Two sets of experiments were conducted. In one, five pentane solutions of DCE plus 1,1,1-trichloroethane (MC) and carbon tetrachloride (CT) were prepared with nominal concentrations of MC and DCE compound at 1.5, 3, 6, 12 and 24 $\mu\text{g/L}$ and CT at 0.4, 0.8, 1.6, 3.2, and 6.4 $\mu\text{g/L}$. MC and CT bracket DCE in the capillary chromatogram analyzed as shown in Figure 25. Also, a second set of standards was prepared in pentane this time with only DCE added at about the same levels as noted above. Each solution was analyzed by the FSOT GC procedure described above and area counts tabulated for each compound. The results are plotted for DCE in Figure 36. Both pure compound and mixed compound solution data fall on the same line, which appears to have a slope of 1.6×10^6 area counts per $\mu\text{g/L}$ of DCE. More significantly, there is an apparent intercept of 13×10^6 counts most probably indicating an artifact in the analysis scheme. The intercept would correspond to an effective blank level of 8.2 $\mu\text{g/L}$, several times the MDL value of 0.4 $\mu\text{g/L}$ determined by the EPA procedure (Table 29).

Under these circumstances, the MDL has no validity and the pragmatic detection limit is determined by the blank value (40).

Conclusions

Detection limits of the LLE method using packed column and FSOT capillary column techniques have been determined. For the brominated THMs, MDL values are in the range of 0.6 - 0.8 $\mu\text{g/L}$; but for chloroform, an MDL of near 3 $\mu\text{g/L}$ is indicated. This is presumably due to variations in blank levels in pentane and in water used for preparing calibration standards.

Other organohalides have MDL values in the range of 0.2 - 0.6 $\mu\text{g/L}$, except for 1,2-dichloroethane, whose MDL is determined by an artifact in the blank at 8 $\mu\text{g/L}$. 1,2-Dichloroethylene may

have a similar high level that was not detected in this study. 1,2-Dichlorobenzene, an example of a compound not currently under active consideration as a drinking water contaminant (2), may also be determined by the 20:1 LLE/GC-ECD method with an MDL of 2 µg/L.

Aromatic compounds determined with the FID have somewhat higher MD values, ranging from 16 to 40 µg/L.

Lower MDL values may be achieved with a higher solvent:water extraction ratio, such as the 240:1 method described in this work. The method has not been thoroughly tested or optimized, and should be used only after appropriate development work.

APPLICATIONS OF THE PENTANE LLE METHOD

Summary of Recommended Method

The method may be used for the following compounds: THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3); 1,1,1-trichloroethane; carbon tetrachloride; 1,2-dichloroethane; trichloroethylene; 1,1,2-trichloroethane; and tetrachloroethylene; benzene; toluene; ethylbenzene; the xylenes; and the dichlorobenzenes. The method may also be extended to other nonpolar organic compounds, particularly those with boiling points above that of chloroform. The method is not recommended for very volatile compounds such as vinyl chloride and the dichloroethylenes, although with special care and some modification, these substances may be included. The method will also measure the dihaloacetonitriles and dichloriodomethane but the analyst should be aware of the difficulties associated with the preparation and preservation of standards, and problems with the stability of these substances in water (38, 42). If trihalomethane formation potential (43) is to be measured, a procedure similar to that described by Glaze *et al.* (44) should be used, in which the chlorination reaction is carried out in the vial to be used for the extraction. At the conclusion of the time required for reaction, quench may be added and the THMs analyzed as described below.

Details of the Procedure--

The extraction procedure is carried out in 25 mL (6 dram) borosilicate vials (Supelco, #2-3257) with screw caps, the tops of which have a 10 mm i.d. perforation. A silicone rubber liner with a Teflon coating on one side (Supelco, #2-3276) is used in conjunction with the cap so that a syringe needle may pierce the liner in order to withdraw or add materials to the vial. The Teflon face of the liner is placed in contact with the sample inside the bottle.

The water sample to be analyzed is usually added to the bottle in such a way as to avoid excessive loss of volatiles, i.e. without much bubbling. The vial is completely filled so that a convex meniscus is seen above the lip of the bottle. For samples which have residual chlorine present or suspected, a chlorine quenching agent is added to the vial before the vial is filled with sample. The nominal amount of quench used in this work was 0.25 mL of a solution containing 0.04 M Na_2SO_3 . Care should be taken in filling the bottle to insure that the quench is not washed out. No buffer is required if the sample is to be analyzed directly, i.e. without further chlorination.

Samples may be stored for several days before analysis providing quenching agent has been added to react with residual chlorine. It is recommended that the samples be stored in the dark at or near 4°C.

On the day samples are to be analyzed, the GC system is properly calibrated using standards prepared by the procedure dictated by EPA (1). A solvent blank should be run to insure adequate purity before the extractions are performed.

Extractions are carried out as described in the Experimental section (Figure 4), by first removing 5.0 mL of water from the vial, then adding 1.0 mL of *n*-pentane. These manipulations are carried out while the bottle remains closed. Care should be taken to make the volumetric measurements as close as possible, as this is probably the most important step determining the overall precision and accuracy of the method.

The pentane used for the extractions should be free of excessive interferences and should contain an internal standard at an appropriate concentration level. The standard used in this work for THMs is 1,2-dibromoethane. Other internal standards which may be used are bromotrichloromethane, 1,4-dibromobutane, and 1-chloro-2-bromopropane. *n*-Decane may be used with the GC/FID method.

Following addition of the pentane, the sample is shaken vigorously in order to reach LLE equilibrium. Shaking for one minute by hand, or thirty seconds with a vortex shaker is sufficient. The vial is then allowed to stand for a few minutes until the two layers thoroughly separate. While awaiting analysis, vials should be stored with topsides down.

When the method is being used for samples where the analytes are well above their detection limits (see previous chapter and below), 2.0 mL of pentane may be used so that the pentane layer is more voluminous and easier to sample for GC analysis.

Calibration standards (spikes into rigorously purified water) and water blanks should be treated and extracted by exactly the same procedure as samples.

GC analysis is carried out by carefully removing a 1-2 μ L aliquot from the pentane layer in the vial, and injecting the aliquot into the GC. In case the laboratory is warm, the vial should be cooled in a refrigerator prior to taking of the aliquot.

The 10% squalane column is recommended for THM analysis, with an SP-1000 or 6% OV-11/4% SP-2100 mixed phase column for confirmation. Detailed descriptions of the columns and GC conditions are given in the Experimental Section.

Organohalides, except THMs or as combined with them, may be analyzed with the mixed phase column, or in some cases with the squalane column. For capillary work, an SE-54 column is recommended, although other more polar phases will probably emerge as superior. Fused silica columns are recommended because of ease in handling.

Quantification of the analytes is carried out by the internal standard method (45); however, the internal standard may be omitted. In this case quantification is carried out by direct comparison of peak heights or areas with those of equal volume injections of standard solutions. Peak areas may be measured by one of several methods (1) but an electronic integrator is recommended. The detector used should be shown to give a response which is linearly proportional to the concentration of the analyte in the range of concentrations measured.

For routine analysis of samples, EPA quality assurance procedures should be followed (32).

Precision of the LLE Method

The LLE extraction method for the analysis of THMs using isothermal, packed column GC with ECD has been the subject of intensive study by both EPA laboratories and contractors. Although the method used here is somewhat different, it is basically the same as that prescribed by EPA (1). The principal differences are the use of slightly different methods for introduction of the solvent, the use of the internal standard method for quantification, and a volumetric ratio $V_w/V_s = 20$, rather than 5, as specified by EPA.

The method described above has been utilized in a three-year EPA sponsored study on THM precursor control (46), and has generally given results which are within $\pm 10\%$ for replicate analysis.

Table 31 shows data which illustrates the typical precision obtained by the method for THM analyses. Again, this refers to isothermal packed column studies with the 20:1 method.

There is considerably less experience available for judging the precision of the capillary GC method with temperature programming. Some understanding in this matter may be derived by an analysis of the data on lower detection limits reported in the previous part of this section. Table 32 shows results of replicate analysis of solutions of eleven organohalides near the detection limit for each. This data shows that the capillary GC/ECD procedure, including the extraction step has a precision of approximately 20%. Average values of S.D., the standard

TABLE 32. PRECISION OF LLE METHOD FOR THMs IN ACTUAL WATER SAMPLES^a

	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
	<u>Texas and Louisiana Cities Waters^b</u>			
Conc. Range (µg/L)	0.7 to 56	0.16 to 40	1.7 to 22	0.65 to 2.0
Median RSD (%)	7.4	14	12	21
N ^c	8	6	4	4
	<u>Denton, Texas Water</u>			
Conc. Range (µg/L)	4 to 90	2 to 50	2 to 25	1.5 to 2.4
Median RSD (%)	7.8	5.7	10	10
N ^c	8	8	8	4

^a Analyzed on the 12.5% squalane column isothermally at 80°C with internal standard, 1,2-dibromoethane.

^b Drinking and other water samples from eight cities in Texas and Louisiana.

^c Number of pairs of samples analyzed.

deviation of replicate analyses, was 19% with a range from 5% (o-dichlorobenzene at 9.68 µg/L) to 44% (tetrachloroethylene at 0.20 µg/L). Variances, defined as the absolute value of the spiked value minus the means of measured values (on a percentage basis), averaged 10% with a range from 0% (carbon tetrachloride at 0.16 µg/L) to 27% (chlorodibromomethane at 1.08 µg/L). Given the fact that these data are near the detection limit, one presumes the precision and accuracy of the method would be superior at higher concentration values.

Analysis of EPA Quality Control Check Sample

Another measure of the precision and accuracy of the capillary GC/LLE method may be obtained from the results of a EPA Quality Control Check (WP 1278). Table 33 shows the data obtained for this check, which consisted of two samples at different concentration levels. Concentration values are reported as determined by the internal standard method with 1,2-dichlorobutane as the standard. The following solvent blank values were subtracted from the observed concentrations: CHCl₃ (0.84 µg/L); 1,1,1-trichloroethane (0.08 µg/L); 1,2-dichloroethane (3.4 µg/L); CCl₄ (0.01 µg/L); C₂Cl₄ (0.04 µg/L).

As expected, the accuracy of the method for 1,2-dichloroethane is poor and the compound could not be verified at the 1.5 µg/L level. The variance for bromoform at the 10.4 µg/L is also higher than one would prefer. However, for all other cases the accuracy of the method is quite acceptable. In all cases the precision of duplicate runs was within +20%, and except for two compounds at the lower concentration level, within +10%.

Analysis of Samples of Drinking Water

In the latter stages of this study, five samples were obtained from the EPA Project Officer for analysis by the LLE method. The samples were extracted by the 20:1 n-pentane method and analyzed by FSOT capillary GC with SE-54 column. Both ECD and FID were used; however, no evidence of aromatic hydrocarbons was observed from the LLE analysis.

In Table 35, concentrations are tabulated for those compounds identified by the HP 5840A data system as having retention times within a window +5% of the calibrated value. Solvent blank values were subtracted from the measured concentration values, and no data were reported if the observed value was below the MDL.

Table 35 also lists concentrations of the organohalides measured with HP 7675A Purge and Trap Module, using the ECD. The

TABLE 33. VARIANCE AND PRECISION OF REPLICATE CAPILLARY GC ANALYSIS OF SPIKED STANDARDS OF ORGANOHALIDES IN WATER

COMPOUND	LOW CONCENTRATION RANGE					UPPER CONCENTRATION RANGE				
	N	Si	Sm	S.D. %	V %	N	Si	Sm	S.D. %	V %
Chloroform	7	2.76	2.53	7	8	8	5.52	5.36	18	3
1,1,1-Trichloroethane	7	0.35	0.32	16	9	9	0.70	0.74	28	5
1,2-Dichloroethane	7	0.57	0.53	9	7	9	1.14	1.24	12	9
Carbon Tetrachloride	7	0.16	0.16	31	0	10	0.32	0.37	27	16
Trichloroethylene	6	0.40	0.39	23	3	10	0.80	0.82	26	3
Bromodichloromethane	6	0.46	0.47	6	2	9	0.92	1.08	19	17
1,1,2-Trichloroethane	-	0.57	nm	nm	nm	9	1.14	1.19	18	4
Chlorodibromomethane	5	0.54	0.59	8	9	9	1.08	1.37	19	27
Tetrachloroethylene	6	0.20	0.18	44	10	9	0.40	0.47	15	18
Bromoform	7	0.40	0.53	25	18	9	0.80	0.98	20	22
O-Dichlorobenzene	nm	4.84	nm	nm	nm	4	9.68	10.01	5	3

N: number of replicate analyses; Si: spiked concentration ($\mu\text{g/L}$); Sm: measured value (mean of N determinations with GC data system calibrated at Si); S.D.: standard deviation, %; $V = \frac{Si - Sm}{Sm} \times 100$; S.D.V.: standard deviation of variance, %; nm: not measurable at this concentration.

TABLE 34. ANALYSIS OF EPA QUALITY CONTROL CHECK SAMPLE #WP 1278 BY THE
PENTANE LLE METHOD WITH FSOT CAPILLARY GC ANALYSIS

COMPOUND	$\mu\text{g/L}$					
	SAMPLE NO. 1			SAMPLE NO. 2		
	EPA Value S_m	S.D.%	V%	EPA Value S_m	% Dev.	% Var.
1,2-Dichloroethane	1.5	b	-	20.0	13.6	4
Chloroform	11.0	11.0	10	45.6	51.2	7
1,1,1-Trichloroethane	1.1	0.9	12	14.0	12.3	6
Trichloroethylene	2.6	2.5	1	13.0	12.9	3
Carbon Tetrachloride	2.3	2.2	1	9.4	9.9	5
Tetrachloroethylene	1.1	1.0	5	5.6	6.0	2
Bromodichloromethane	1.7	1.7	0	8.6	10.0	4
Chlorodibromomethane	2.4	2.2	5	12.0	12.2	3
Bromoform	2.8	2.9	1	10.4	13.6	8

S_m : mean of duplicate runs (separate extractions and analysis); S.D.%: percent deviation of duplicate runs; $V\%$: EPA Value - S_m /EPA value x 100.;
b: below blank level (FSOT capillary column with SE-54 phase; 0°C, 3 min; 3°/min + 120°C; splitless injection, other conditions in text.)

purge and trap procedure is inherently more sensitive than the LLE method, and combined with the ^{63}Ni detector, is a powerfully sensitive method for organohalides. Studies of the purge and trap:ECD combination described earlier in this section show that the linear range for the organohalides is quite limited. Therefore, in the analysis of the samples listed in Table 35, dilution of the water samples was required. By necessity, this is a trial and error procedure which is time consuming and which leads to larger uncertainties than the usual purge and trap:Hall method (1).

Moreover, the dilution process introduces higher blank levels of organohalides, as shown in Table 36. Therefore, in deciding the value to be reported, some discretion was required. Chloroform was reported only as determined from undiluted runs because of high blanks in dilution water. All others were reported at the lowest dilution level except when it was suspected that the linear range of the detector was exceeded.

Table 35 shows reasonably good agreement between the purge and trap and LLE methods with some notable irregularities. The trichloroethylene values for sample 0880-35-09 are badly out of agreement, and there are other similar cases involving bromoform and tetrachloroethylene. It is suspected that the cause may lie in the integrated areas reported by the HP 5840A reporting integrator. Slope sensitivity settings are particularly critical so as to avoid excessive false integrated areas of broad peaks at the end of chromatograms. This is a factor which speaks for a more simple peak measuring method, especially in the hands of technicians with lower skill factors. Finally, it should be recorded that purge and trap:FID analysis of the samples showed 0618-07-02 contained 7.1 ± 0.7 $\mu\text{g/L}$ benzene and sample 0880-35-09 showed a peak near the retention time of benzene but outside the 5% window for identification. No other significant amounts of hydrocarbons were detected.

Conclusions

The precision of the 20:1 pentane LLE method as practiced in this work was usually within $\pm 20\%$.

Two EPA QC samples containing nine volatile organohalides were analyzed by the LLE method with capillary FSOT GC columns. Except for 1,2-dichloroethane, and in one case for bromoform, reported values were within 18% of the true values. Average variance from the true value was $\pm 6\%$ for the low concentration sample (excluding 1,2-dichloroethane), and $\pm 13\%$ (including all nine compounds) for the high concentration sample.

Analysis of five samples of water supplied by EPA was carried out by the LLE method with FSOT/GC and by the purge and trap method with ECD and FID. In general, the results obtained by the two methods were close to each other, with a few notable exceptions. With the ECD the purge and trap module is so sensitive for organohalides that dilutions of the samples were required. This is a laborious procedure which in some cases may result in poor precision and accuracy. No hydrocarbons were observed by LLE, but benzene was quantified at 7 $\mu\text{g/L}$ in one sample by purge and trap:FID.

TABLE 35. ILE/CAPILLARY GC AND PURGE AND TRAP ANALYSIS OF DRINKING WATER SAMPLES

 $\mu\text{g/L}$

COMPOUND	DETECTION LIMIT		BLANK VALUE		0202-13-13		0618-07-02		0737-38-13		0314-16-11		0880-35-09	
	ILE	P/T	ILE	P/T	ILE	P/T	ILE	P/T	ILE	P/T	ILE	P/T	ILE	P/T
Chloroform	2.9	0.4	0.8	0.4	-	-	-	-	0.73 $\pm$ 0.02	-	3.6 $\pm$ 0.4	4.2	4.7 $\pm$ 4	4.7 $\pm$ 0.1
1,1,1-Trichloroethane	0.6	0.1	0.08	0.1	1.9 $\pm$ 0.1	1.7 $\pm$ 0.4	1.7 $\pm$ 0.1	2.0 $\pm$ 0.06	10.5 $\pm$ 0.6	9.0 $\pm$ 0.5	-	-	-	0.4 $\pm$ 0.03
1,2-Dichloroethane	8	0.05	8	0.05	-	0.25 $\pm$ 0.03	1.6 $\pm$ 0.1	3.4 $\pm$ 0.03	0.1 $\pm$ 0.02	2.3 $\pm$ 0.09	0.45 $\pm$ 0.02	2.8 $\pm$ 0.2	2.2 $\pm$ 0.2	-
Carbon Tetrachloride	0.3	0.1	0.01	0.1	-	-	-	-	-	-	3.9 $\pm$ 0.2	4.0 $\pm$ 0.2	-	-
Bromodichloromethane	0.6	0.06	-	0.06	-	-	-	0.16 $\pm$ 0.004	1.1 $\pm$ 0.1	1.23 $\pm$ 0.03	14.0 $\pm$ 0.9	11.9 $\pm$ 0.1	7.2 $\pm$ 0.1	3.0 $\pm$ 0.1
Dibromochloromethane	0.8	0.2	-	0.2	-	-	-	0.7 $\pm$ 0.02	3.0 $\pm$ 0.3	4.7 $\pm$ 0	30.1 $\pm$ 1.8	33.3 $\pm$ 0.2	6.2 $\pm$ 0.4	5.6 $\pm$ 0.1
Trichloroethylene	0.6	0.2	-	0.2	4.32 $\pm$ 0.03	1.7 $\pm$ 0.1	-	0.20 $\pm$ 0.01	2.76 $\pm$ 0.03	3.5 $\pm$ 0.05	-	0.74 $\pm$ 0.01	29.7 $\pm$ 0.8	4.1 $\pm$ 0.1
Tetrachloroethylene	0.2	0.01	0.04	0.01	0.39 $\pm$ 0.02	0.38 $\pm$ 0.04	-	0.12 $\pm$ 0.01	2.7 $\pm$ 0.3	2.9 $\pm$ 0.4	1.8 $\pm$ 0.5	0.9 $\pm$ 0.2	0.28 $\pm$ 0.02	0.10 $\pm$ 0.05
Bromoform	0.6	0.005	-	0.005	-	-	12.3 $\pm$ 0.6	5.7 $\pm$ 0.3	3.8 $\pm$ 0.3	3.4 $\pm$ 0.1	28.0 $\pm$ 1.7	16.6 $\pm$ 1.6	3.1 $\pm$ 0.1	1.0 $\pm$ 0.1
Benzene	-	-	-	-	0.89 $\pm$ 0.05	-	-	7.1 $\pm$ 0.8	-	1.0 $\pm$ 0.1	-	-	-	-
Toluene	-	-	-	-	-	-	-	0.12 $\pm$ 0.04	-	0.08 $\pm$ 0.001	-	-	-	-
O-Dichlorobenzene	-	-	-	-	-	-	-	0.33 $\pm$ 0.02	-	-	-	-	-	-

ILE: 20/L Pentane microextraction with GC/EC or GC/FID; 30 m x 0.25 mm i.d. FSO7/SE-54; 0°, 3 min; 3°/min to 120°
 Purge 75 ml. sample; 10 min He purge at 40 ml/min; desorption, 250°, 0.2% Carbowax 1500 on 80/100 Carbowax; organochalides: column at 60°, 3 min,
 & Trap 3°/min to 130°, BCD; aromatics: column at 130°, 3 min, 15°/min to 160°, FID.
 Blank values subtracted. No values reported below detection limits listed in Tables 30 and 31.

TABLE 16. PURGE AND TRAP-ECD ANALYSIS OF EPA DRINKING WATER SAMPLES - EFFECT OF DILUTION^a

COMPOUND	0202-13-13		0618-07-02		0737-38-13		0314-16-11		0880-35-09		
	$\frac{b}{u}$	1/2	$\frac{b}{u}$	1/10	u	1/10	u	1/5	1/25	u	1/25
Chloroform	-	-	-	3.1±0.6	0.73±0.02 ^b	3.2±0	4.2	5.7±0.03 ^b	12.6±1.6	4.7±0.1 ^b	14.6±2.0
1,1,1-Trichloroethane	1.7±0.4	1.4±0.01	2.0±0.06	2.9±0.2	6.5±0.2	9.0±0.6 ^b	a	a	a	0.4±0.03 ^b	4.2±.3
1,2-Dichloroethane	0.16±0.02	0.25±0.03	0.91±0.03	3.4±0.03	0.11±0.02 ^b	0.8±0.03	-	0.45±.02 ^b	2.0±0.2	a	2.2±0.2 ^b
Carbon Tetrachloride	-	-	u	0.5±0.2	-	-	4.5	4.0±.2 ^b	6.2±1.2	-	-
Bromodichloromethane	-	-	0.16±.004	0.5±0.02	1.2±0.03 ^b	1.7±0.1	-	11.9±.1 ^b	17.1±.5	3.0±0.1 ^b	7.7±0.2
Dibromochloromethane	-	-	0.7±0.02	3.1±0.1	2.7±0.1	4.7±0 ^b	9.8	33.4±0.2 ^b	58±2	5.6±.1 ^b	15.7±.4
Trichloroethylene	1.7±0.1	1.5±0.1	0.20±.006	2.6±0.07	1.1±0.003	3.5±0.05 ^b	0.31	0.74±0 ^b	3.4±0.1	4.1±.1 ^b	11.5±.3
N ₂ Tetrachloroethylene	0.38±0.04	0.39±0.07	0.12±0.01	1.1±0.3	1.5±0.2	2.9±0.4 ^b	0.35	0.9±0.2 ^b	3.5±0.4	0.1±0.05 ^b	2.8±0.2
Bromoform	-	-	2.5±0.1	5.7±0.3 ^b	1.2±0.1	3.4±0.1 ^b	5.6	10.1±.5	16.6±1.6 ^b	1.0±.1 ^b	6.8±.8

^au: undiluted; 1/2: dilution factor, i.e. 1 volume of sample diluted to 2 volumes with reagent water^bReported in Table^aUnresolved peak

REFERENCES

1. Federal Register, 44(231), 68683 (1979).
2. Federal Register, 47(43), 9350 (1982).
3. Garrison, A.W., Alford, A.L., Craig, J.S., Ellington, J.J., Haebeler, A.F., McGuire, J.M., Pope, J.D., Shackelford, W.M., Pellizzari, E.D., Gebhart, J.E., in Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 1, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 17-30 (1981).
4. Grob, K., Grob, K., Jr., Grob, G., J. Chromatography, 106, 299-315 (1975).
5. Rook, J.J., J. Water Treat. Exam., 23, 234 (1974).
6. Nicholson, A.A. and Meresz, O., Bull. Environ. Contam. Toxicol., 14, 453 (1975).
7. Schenk, G.H., Hahn, R.B., Hartkopf, A.V., Quantitative Analytical Chemistry, Allyn and Bacon, Inc., Boston, MA. 433-442 (1977).
8. Junk, G.A., Ogawa, I., Srec, H.J., in Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 1, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 281-292 (1981).
9. Thoades, J.W., Nulton, C.P., J. Environ. Sci. Health, A15, 467-484 (1980).
10. Rhoades, J.W., Nulton, C.P., in Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 1, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 241-252 (1981).
11. Rhoades, J.W., Millar, J.D., J. Agr. Food Chem., 13, -9 (1965).
12. Blanchet, P.-F., J. Chromatography, 179, 123-129 (1979).
13. Thrun, K.E., Simmons, K.E., Oberholtzer, J.E., J. Environ. Sci. Health, A15, 485-501 (1980).

14. Henderson, J.E., Peyton, G.R., Glaze, W.H., in Identification and Analysis of Organic Pollutants in Water, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 105 (1975).
15. Mieure, J.P., J. Am. Water Works Assoc., 69, 60 (1977).
16. Richard, J.J., Junk, G.A., J. Am. Water Works Assoc., 69, 62 (1977).
17. Glaze, W.H., Rawley, R., Burleson, J.L., Mapel, D., Scott, D.R., in Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 1, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 267-280 (1981).
18. Thrun, K.E., Oberholtzer, J.E., in Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 1, L.F. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 253-266 (1981).
19. Eklund, G., Josefsson, B., Roos, C., in "Recent Advances in Capillary Gas Chromatography", W. Bertsch, W.G., Jennings, and R.E. Kaiser, Editors, Huthig Verlag, Heidelberg, 533-550 (1981).
20. Friestad, H.O., J. AOAC, 60, 268-271 (1977).
21. Murray, D.A.J., J. Chromatography, 177, 135-140 (1979).
22. American Chemical Society, Committee on Environmental Improvement, "Data Acquisition and Data Quality Evaluation in Environmental Chemistry", Analytical Chemistry, 52, 2242-2248 (1980).
23. U.S. Environmental Protection Agency, "Contractors Engineering Report: Analysis of Organic Chemicals and Plastics/Synthetic Fibers Industries", Effluent Guidelines Division, Washington, D.C., Contract No. 68-01-6024, November 16, 1981.
24. Reding, R., Kollman, W.B., Weisner, M.J., Brass, H.J., Proceedings of the Symposium on Measurement of Organic Pollutants in Water and Wastewater, ASTM Comm. D-19 on Water, June 19-20 (1978).
25. Bellar, T.A.,; Lichtenberg, J., J. Am. Water Works Assoc. 1974, 66, 739.

26. Smith, V.L., Cech, I., Brown, J.H., Bogdan, G.F., Environ. Sci. Tech., 14, 190-196 (1980).
27. Oliver, B.G. Shindler, D.B., Environ. Sci. Tech., 14, 1502-1505 (1980).
28. Olson, R., Williams, D.T., Bothwell, P.D., Environ. Sci. Tech., 13, 936-939 (1979).
29. Croll, B.T., in "Trihalomethanes in Water Seminar", Papers and Proceedings, Water Research Center, Medmenham Laboratory, England, 27-48 (1980).
30. Trussell, A.R., Cromer, J.L., Umphres, M.D., Kelley, P.E., Moncur, J.G., in "Water Chlorination: Environmental Impact and Health Effects", R.L. Jolley, W.A. Brungs and R.B. Cumming, Editors, Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 39-53 (1980).
31. Henderson, J.E. Ph.D. Dissertation, North Texas State University, Denton, Texas (1982).
32. U.S. Environmental Protection Agency, "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA-600/4-79-019, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, Section 9 (1979).
33. Dandeneau, R., Zerenner, E.H., J. High Resolution Chromatog., Chromatog. Commun., 3, 351 (1979).
34. Freeman, R.R., in "Advances in the Identification and Analysis of Organic Pollutants in Water", Vol. 1, L.H. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 155-170 (1981).
35. Trussell, A.R., Lieu, F.-Y., Moncur, J.G., ibid., 171-186 (1981).
36. Grob, K., Grob, K., Jr., in "Recent Advances in Capillary Gas Chromatography", W. Bertsch, W.G. Jennings, R.E. Kaiser, Eds., Huthig Verlag, Heidelberg, 455-473 (1981).
37. McKinney, J.D., Mauer, R.R., Hass, J.R., Thomas, R.O., in "Identification and Analysis of Organic Pollutants in Water", L.H. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 417 (1976).

38. Trehy, M.L., Bieber, T.I., in "Advances in the Identification and Analysis of Organic Pollutants in Water", L.H. Keith, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 941-975 (1981).
39. Kaiser, H.H., Anal. Chem., 42, 26A (1970).
40. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., Budde, W.L., Environ. Sci. Tech., 15, 1426-1435 (1981).
41. U.S. Environmental Protection Agency, "Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.12", Environmental Monitoring and Support Laboratory, Cincinnati, OH., January, 1981.
42. Thomas, R.F., Weisner, M.J., Brass, H.J. in "Water Chlorination: Environmental Impact and Health Effects", Vol. 3, R.L. Jolley, W.A. Brungs and R.G. Cumming, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 161 (1980).
43. Stevens, A.A.; Symons, J.M., J. Amer. Water Works Assoc., 69, 546-554 (1977).
44. Glaze, W.H., Wallace, J.L., Dickson, K.L., Wilcox, D.P., Johannson, K.R., Chang, E., Busch, A.W., Scalf, B.G., Noack, R.K., Smith, D.P. Jr., "Evaluation of Biological Activated Carbon for Removal of Trihalomethane Precursors", Final Report, EPA Cooperative Agreement CR806157, MERL, Cincinnati, OH (1981).
45. Hewlett-Packard Corporation, Manual for the 5840A Gas Chromatograph, Methods", 1820 Embarcadero Rd., Palo Alto, CA 94303.